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DEVELOPMENT OF SILVER NANOCUBES CREATED BY PULSED LASER ABLATION IN LIQUID

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This research work describes a simple approach for creating silver (Ag) nanocubes using pulsed laser ablation in a liquid medium. The development of nano cubical formations of Ag obtained by laser ablation using Nd: YAG laser was conducted for 5, 10, 15, and 20 minutes. The surface morphological analysis was performed using field-emission scanning electron microscopy (FESEM) to show the formation of silver nanocubes with edge lengths ranging from 150 nm to 250 nm. The UV-visible spectroscopy demonstrates that the concentration of Ag nanostructures, evidenced by the characteristic localized surface plasmon resonance band near 400 nm, in the colloidal solution containing Ag nanoparticles, increased with the increasing laser ablation duration from 5 to 20 minutes. The growth mechanism for Ag nanocubes can be easily understood with the change in laser ablation time from 5 to 10, 15, and then 20 minutes. The Ag sheets with no specific shape start to develop after 5 minutes of laser ablation, and after 10 minutes, larger particles form. Then, after 15 minutes, a small number of cube-like nanostructures with rough and uneven edges was obtained. At the end of 20 minutes, a full cubic form with fine and distinct edges and a very large amount of nanocubes. The elemental silver signal was found to be present in Ag nanocubes, as revealed by the energy-dispersive x-ray spectroscopy (EDS) spectra. The produced Ag nanocubes may be used to construct two-dimensional nanocomposites with practical applications in the electrical, optoelectronic, electrochemical, and biological areas.

Keywords: Laser ablation; silver nanoparticles; optical properties, growth mechanism.

1. Introduction

Noble metal nanoparticles have garnered interest and popularity in the field of materials science and nanomaterials synthesis. This interest enhances with every passing year because of their impactful properties, which are very different from bulk materials. Among
divergent nanocrystals, Ag nanoparticles (Ag-NPs) have become the center of attention in different research owing to their optical, electronic, magnetic, and antibacterial properties which highly contradict the bulk counterpart. Silver nanoparticles with different shapes,

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like nanocubes, have very good optical and electromagnetic properties with well-defined geometric. Both the size and shape of nanoparticles have a great impact on the application and effectiveness. The size has an impact on the uptake efficiency and kinetics, mechanism process, and sub-cellular dispersion. Also, the size and surface morphology have an important role in properties, with the high surface energy of the nanoparticles they become highly reactive[1]. The nanocubes have localized surface plasmon resonance (LSPR), which can be finely tuned by altering morphology and composition, which makes this an important nanomaterial to use in surface-enhanced Raman spectroscopy (SERS), biosensing, non-linear optics, catalyst and drug delivery [2]. Silver nanoparticles are highly effective as anti-bacterial agents both gram-positive and negative [3], in medical applications as anticancer, antimicrobial agents, and bio-safety [4], in textile fabric coatings [5], in agriculture as pesticides and growing crops yield [6-7], water contamination monitoring as well as treatment, ecosafe application [8]. In addition, the controlled size of silver nanoparticles, to be precise nanocubes are highly useful in terms of LSPR and SERS, meta-materials (Ag and Au), seeds for further growth, and catalysis [9].

Numerous articles detailing the production of Ag nanocubes and their constituents, each of which displays distinctive features, have been published up to the present day. Qiang Zhang, et al. showed that the seeded growth technique can be used to produce silver nanocubes with edge lengths varying from 30 to 200 nm [10]. This study reveals the size dependency of LSPR and SERS characteristics for Ag nanocubes with precise control over on size to create the optimal SERS substrate. While nanocubes composed of Ag were successfully produced with a precisely controlled size range of 18-32 nm as demonstrated by Yi Wang et al. [11]. The synthesis process featured diethylene glycol (DEG) as a solvent, distinguished by its hydrocarbon chain length, high viscosity, and relatively reduced reduction power. This characteristic facilitates the occurrence of a nucleation burst characterized by a substantial quantity of seeds and consequently slower growth rate. This approach is effective enough to remove contaminants with high sensitivity. While in another research, a template-assisted reduction method was used to create silver cubic form mesh nanostructures embedded with gold nanoparticles using AgCl templates. The plasmonic photocatalysis of cubic mesh nanostructures enhances that of traditional TiO_2 catalysts due to their large surface area and exceptional chemical stability [12]. Jiafeng He et al. have shown the efficient production of silver nanocubes and graphene oxide composites for sensitive SERS detection of various organic pollutants including malachite green, MB, and crystal violet [13]. The sensitive detection is facilitated by the electromagnetic field effect emerging from Ag nanocubes and the chemical enhancement of graphene oxide sheets. Ag nanocubes-GO composites have shown the ability to establish a highly sensitive and uniform surface-enhanced Raman scattering (SERS) platform. This platform has great potential for applications in the fields of food safety monitoring and environmental investigations. Jian-Jia Liu et al. have conducted a study on the preparation of two heterogeneous nanocomposites, one with a core-shell MOF-AgNC morphology and the other with a corner MOF-AgNC morphology with the purpose of serving as photocatalysts to decrease CO_2 [14]. The MOF located in the corner of MOF-AgNC nanocomposite has a greater surface-to-volume ratio contributing to the

faster CO_2 adsorption rate that was observed in the corner MOF-AgNC nanocomposite in comparison to the core-shell MOF-AgNC nanocomposite. The synthesis of heterogeneous nanocomposites serves the purpose of enabling the development of photocatalysts for various processes via the precise control of the shape and composition of such nanocomposites.

Among various methods to be used in nanoparticle synthesis, pulsed laser ablation in liquid (PLAL) is a green, simple, straightforward, fast, and low-cost process with being unconventional because this process does not need a very long reaction time, multiple steps, and temperature [15-16]. PLAL is also a green synthesis process without the involvement of chemicals [17]. This study presents a simple Ag nanocubes manufacturing procedure employing pulsed laser ablation in water using Nd: YAG laser operating at 532 nm and having a pulse length of 10 ns. The pulsed laser was irradiated vertically on the silver solid plate that emerged in water for different laser ablation times to identify the growth of nano-shapes with increasing time. By utilizing UV-visible spectroscopy the growth mechanism was monitored and the morphological change was observed by field electron scanning electron microscope (FE-SEM). In addition, SEM-EDS was used to find the elemental mapping of the nanocubes.

2. Experimental

Careful synthesis of Ag cubic nanostructures in a liquid environment using laser ablation has great potential for cutting-edge material science. The experimental framework entailed the utilization of a cutting-edge Q-switched Nd:YAG nanosecond laser system (Spectra-Physics Quanta-Ray) with a finely tuned pulse duration of ~ 10 ns (full-width half maximum - FWHM). The laser, operating at a wavelength of around 532 nm, delivered a precisely controlled pulse power of approximately 600 mW, exhibiting a repetition frequency of ~10 Hz.

A solid Ag sheet (Nilaco Corp., Japan), possessing dimensions of 2 cm × 2 cm × 2 mm, was placed on the bottom of 20 mL distilled (DI) water as shown in Fig. 1 . This crucial step of the experiment was vertical laser irradiation, with the laser power maintained at 600 mW. Four distinct durations 5, 10, 15, and 20 minutes were selected, encompassing a comprehensive exploration of the process kinetics.

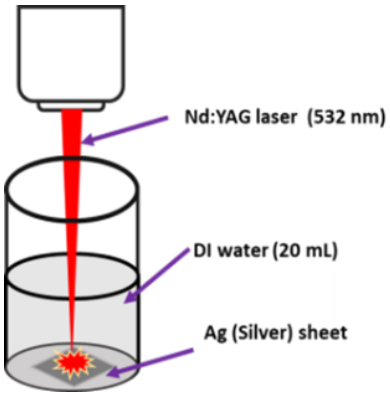

Fig 1: Schematic of laser ablation set up for synthesis of Ag nanocube

Following the completion of each ablation duration, the morphological features of the Ag colloidal solutions were meticulously characterized utilizing field-emission scanning electron microscopy (FESEM) techniques (JEOL JSM-6510) operating at an accelerated voltage of 200 kV.

To better understand the spectral characteristics of the laser-ablated Ag colloidal solution, UV-visible spectra were meticulously recorded using a highly precise V-670 (JASCO-Japan) spectrometer. Furthermore, a sophisticated scanning electron microscopy setup equipped with energy-dispersive X-ray spectroscopy (SEM-EDS) was utilized. This advanced analytical approach facilitated elemental mapping of the nanocubes within the colloidal solution with 20 minutes of laser ablation, enabling a comprehensive understanding of the elemental distribution and composition. To ensure the structure and generation of Ag, X-ray diffraction (XRD, Miniflex600, Rigaku) spectroscopy for each of four different durations was employed which confirms the presence of Ag nanoparticles

3. Results and Discussion

3.1. *UV-visible spectroscopy*

When it comes to the optical characterization of nanoparticles, one of the most extensively used method is called UV-visible spectroscopy. Using UV spectroscopy technique, it is well known that the typical surface plasmon resonance (SPR) band for Ag nanoparticles can be found at 400 nm [18]. Figure 2 (a) shows the UV-visible spectra of Ag nanoparticles produced by increasing the laser ablation time.

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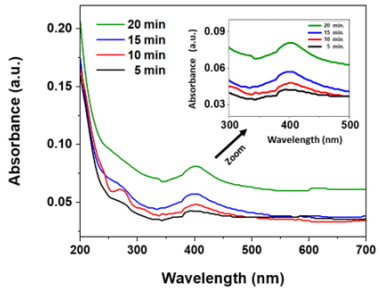

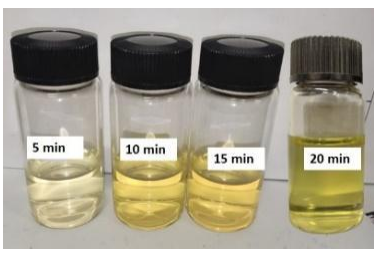

Fig. 2(a) : UV-Visible spectra of Ag nanoparticles for 5, 10, 15 and 20 minutes

Fig. 2(b): Photo of Ag nanoparticles for 5, 10 15 and 20 min. laser ablation

With the increment of laser ablation time starting from 5 mins to end with 20 mins with the extension of 5 mins for each sample, synthesis of silver nanoparticles increases with the increment of time as evidenced by the increase in absorbance band at 400 nm. For all four absorption spectra, the peak can be seen near 400 nm which is the characteristic peak for Ag as reported earlier [10].

Following a preliminary laser ablation duration of 5 minutes, the absorption peak exhibited an approximate magnitude of 0.04 as can be seen in the inset of Fig 2(a). Subsequently, this magnitude augmented to approximately 0.05 after a 10 minutes ablation period. Following another increment of 5 minutes in the ablation time, the peak intensity further peak intensity that escalated to nearly 0.08. This significant augmentation in the UV peak intensity provides evidence for the hypothesis of progressively augmented Ag nanoparticle accumulation with the increase in ablation time, thus substantiating the advancement toward a well-defined formation process. However, for all samples, the wavelength remains almost constant at 400 nm.

Through a time-resolved investigation, we discern distinct color transitions in the solution at different growth stages. Figure 2 (b) demonstrates the color of solutions at different times, Initiating with a faint yellow at 5 minutes of laser ablation that seems almost white with a tint of yellow, then a translucent yellow shade at 10 minutes, with stable yellow color from 15 minutes, culminating in a very light yellow hue at 20 minutes. These color variations signify the progressive formation of Ag nanocubes with unique optical properties [19].

3.2 X-Ray Diffraction :

Figure 3 demonstrates the XRD analysis of Ag nanoparticles after 20 minutes of pulsed laser ablation in water. The XRD spectra revealed many peaks that are indicative of the formation of Ag nanoparticles. which are connected to diffraction from the (122), (111), (200) crystallographic planes of pure silver. These planes are associated with the face-centered cubic structure (JCPDS, file No. 04-0784) [20]. From the inset image, it is the schematic of Ag cube indicating the crystallographic planes which determine that the obtained nanoparticles are crystalline in nature [21].

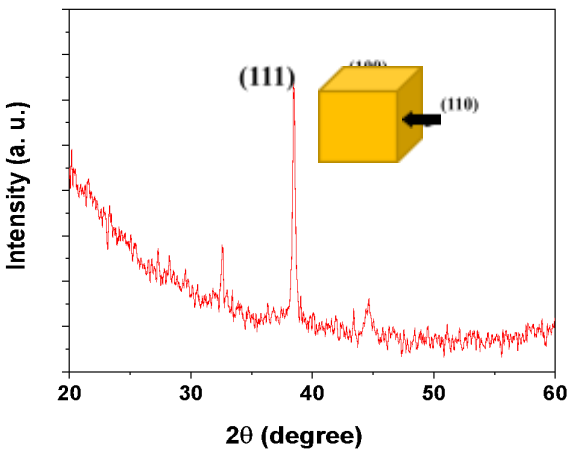

Fig. 3. XRD pattern of the Ag nanoparticles after laser ablation for 20 minutes

3.3 FESEM Analysis

The structural characterization revealed that Ag colloidal solution prepared in a liquid environment exhibits cubic shape nanoparticles as shown in Fig. 4. It is clear that small particles or sheets with different sizes and shapes were present without any definite shape after 5 minutes of laser ablation. Then, after another 5 minutes of laser ablation which is 10 minutes of vertical laser irradiation, the nanoparticles initiated taking

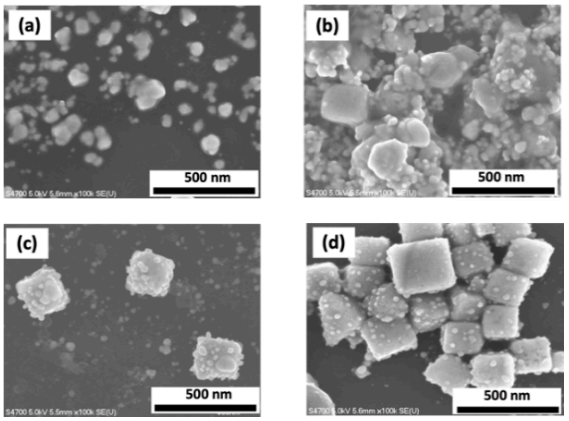

Fig. 4. FESEM images of Ag nanocubes (a) 5 min. (b) 10 min. (c) 15 min. (d) 20 min. laser ablation

shapes with the increase in size becoming bigger particles. This phenomenon shows that Ag particles are agglomerating on the seeds synthesized before. After laser ablation for 15 minutes, the transformation to a cubic shape can be seen, yet the edges of the nanocubes are not very clear and the count of nanocubes is less number. Finally, after 20 minutes of pulsed laser ablation complete transformation to a cubic shape with higher concentration of Ag nanocubes as well as with very sharp and clear edges [22].

3.4 SEM-EDS analysis:

Fig. 5 presents the SEM-EDS outcomes gained from Ag colloidal solution subjected to a voltage of 15 KV. The SEM micrograph depicts well-defined cubic morphologies of Ag particles, which were created from the solution of 20 minutes duration of laser ablation. These cubic structures exhibit a notably higher concentration and distinct geometric regularity.

Analysis of the EDS spectra reveals pronounced peaks corresponding to Ag within the colloidal solution. This observation proves the presence of a substantial amount of Ag content within the solution, as evidenced by the discernible intensity of Ag-related peaks in the EDS spectrum. In addition, the elemental mapping images unveil Ag and chlorine (Cl) distributions. The presence of Cl can be attributed to the utilization of distilled water during the laser ablation process. Furthermore, silicon (Si) presence is discernible in the elemental mapping, stemming from the utilization of a silicon substrate for the deposition and analysis of the colloidal solution. Collectively, these findings collectively affirm the abundant presence of Ag nanocubes within the colloidal solution, characterized by its high concentration and distinctive morphological attributes [23].

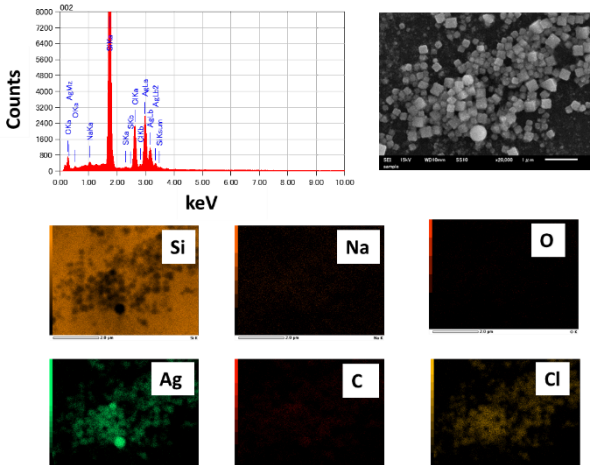

Fig.5. SEM images of Ag Nanocubes EDS spectra with elemental mapping of laser ablated for 20 minutes

3. 5 Growth Mechanism:

The present study was conducted to reveal the synthesis of Ag nanocubes with a simple and green process as laser ablation and go through the whole process of gaining a shape like cubes and how it forms with change in time for laser ablation. According to the experiment, with the increment of time for laser ablation by keeping other parameters such as temperature, laser power, and wavelength certain, changes in the shape of synthesized Ag nanoparticles are obtained. Starting from 5 and reaching to 20 minutes the perfect formation of nanocubes was established.

To reveal the growth mechanism of the nanocubes several analyses were done such as from Fig. 3 to Fig. 5. The process of formation of Ag nanocubes at different laser ablation times with the creation and changes of the shape and density of nanoparticles after every 5 minutes becomes clear as illustrated in Fig. 6. After only 5 minutes of laser ablation, many sheets and undefined structured nanoparticles were seen, yet with the increase of time to 10 minutes the shapes start getting a look and also the size of the particles increased which indicated that new particles from irradiation are agglomerating on the seeds or nuclei created. After 15 minutes, cubic shapes are visible clearly however the amount remains very less in number, and also edges of the shape are still unclear and rounded. Then 20 minutes of laser ablation gives full sharp edge nanocubes with very high concentration.

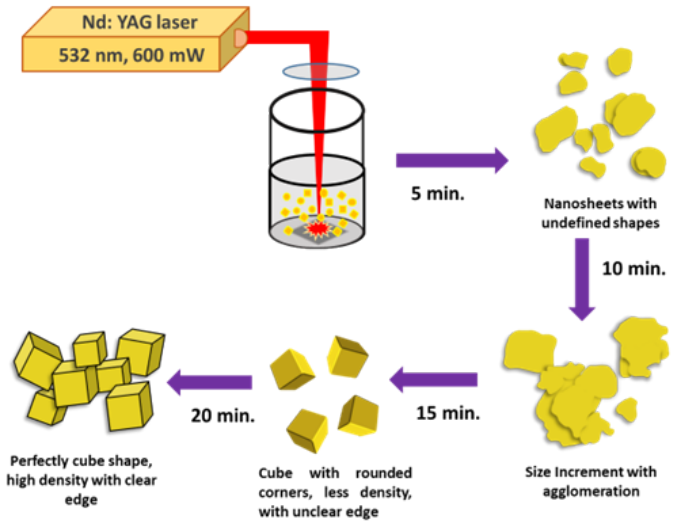

Fig. 6. Schematic of Ag nanocubes synthesis for 5 to 20 minutes with laser ablation in water

To prove the increase in the concentration of nanoparticle synthesis, UV-visible spectroscopic analysis was done for four samples. From Fig. 1, it becomes extremely visible that, the intensity keeps on increasing after every 5 minutes substantiates that more nanoparticles are created every time finally giving high concentration and perfect cube shape of Ag.

4. Conclusions:

Through this study, we provided a comprehensive investigation into the growth mechanism of silver (Ag) nanocubes produced by pulsed laser ablation in water as a liquid medium. In the experiment, the resultant product was well defined Ag nanocubes with varying edge lengths from 150 to 250 nm within the progress of time from 5 minutes to 10 minutes. The optical properties analyzed by UV-visible spectroscopy revealed progress in Localized surface plasmon resonance near 400 nm with the increase of time, which shows enhancement in nanoparticle concentration. In addition, FESEM images confirm the transformation process from undefined structures to well-formed nanocubes

after laser irradiation for 20 minutes. Here, SEM-EDS substantiates Ag presence and the XRD pattern confirms the crystalline nature of synthesized nanoparticles. Thus, this study contributes to advancing nanomaterial synthesis and gives the foundation for the fabrication of nanoparticles with certain properties and understanding of the formation process.

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