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Non-spherical aluminum nanoparticles fabricated using picosecond laser ablation

A. Brahma Swamulu1,3), S. Venugopal Rao2), and G. Krishna Podagatlapalli3)

1) Department of Physics, Rajiv Gandhi University of Knowledge Technologies, Nuzvid, Andhra Pradesh 521202, India
2) Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad, Hyderabad 500046, Telangana, India
3) Department of Electronics & Physics, Gandhi Institute of Technology and Management Institute of Science, Gandhi Institute of Technology and Management deemed to be University, Visakhapatnam 530045, Andhra Pradesh, India

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Abstract: We report the picosecond laser ablation of aluminum targets immersed in a polar organic liquid (chloroform, CHCl3) with ~2 ps laser pulses at an input energy of ~350 μJ. The synthesized aluminum nanoparticles exhibited a surface plasmon resonance peak at ~340 nm. Scanning electron microscopy images of Al nanoparticles demonstrated the spherical morphology with an average size of (27 ± 3.6) nm. The formation of smaller spherical Al nanoparticles and the diminished growth could be from the formation of electric double layers on the Al nanoparticles. In addition to spherical aluminum nanoparticles, triangular/pentagonal/hexagonal nanoparticles were also observed in the colloidal solution. Field emission scanning electron microscopy images of ablated Al targets demonstrated laser induced periodic surface structures (LIPSSs), which were the high spatial frequency LIPSSs (HSF-LIPSSs) since their grating period was ~280 nm. Additionally, coarse structures with a period of ~700 nm were observed.

Keywords: ablation; picosecond; silver; polar; periodic surfaces; electric double layers

1. Introduction

In the last few decades, many physical and chemical methods, such as ball milling, sputtering, sol−gel method, physical vapor deposition, and laser ablation, have been introduced to synthesize nanoparticles and nanostructures. Laser ablation of metal targets results in the formation of nanoparticles (NPs) [1−9]. When ablation occurs in air there will always be the likelihood of contamination of the medium due to the expulsion of nanoparticles. This disadvantage can be fixed by performing the ablation by keeping the metal target in a liquid, thereby restraining the plasma. Laser ablation of metal targets (aluminum, gold, silver, platinum, etc.) immersed in a liquid medium has gained more attention by the scientific community due to its simplicity and versatility. This technique enables the fabrication of nanoparticles and nanostructures in a single experiment, which is only in a few minutes. When a target immersed in a liquid is irradiated by an intense laser light, a metallic plume will be produced on the target surface due to local heating. Subsequently, a liquid layer adjacent to the metallic plume gets evaporated; consequently, it exerts a recoil pressure on the metallic plume that splashes into spherical particles and releases into the liquid in which ablation is taking place. Nanoparticles can be obtained in colloidal form and laser ablation is the only physical technique that produces nanoparticles and nanostructures with a desired roughness in a single experiment. Unlike existing wet chemical methods, laser ablation in liquids does not need vigorous sample preparation or surfactants.

Laser−matter interaction in laser ablation is a complicated phenomenon that occurs underneath the liquid layer. The laser−matter interaction simultaneously depends on the laser parameters, liquid parameters, and inherent characteristics of the metal target. One more advantage of the laser ablation of metals in a liquid media is the possibility of gram scale green synthesis. Laser ablation of metallic targets in a liquid medium significantly depends on the polarity of the liquid. When ablation is carried out in a polar medium [10−12], molecules of the liquid in which ablation is being conducted will be adsorbed on the fabricated primary nanoparticles formed initially. The outcome of the laser ablation is comprised of ions, molecular clusters, atoms, and other com-
stitions. Thus, the produced primary nanoparticles grow by
the nucleation of ions in the cavitation bubble (CB). This
growth mechanism determines the average sizes and shapes
of the nanoparticles in the colloidal solution. During the
growth process, atomic clusters get closer and will attach to
pre-existing nanoparticles.

The growth of nanoparticles or secondary nucleation is
determined by the charge on the surface of primary nano-
particles. If the charge on the primary nanoparticles is posi-
tive or negative, growth is significant due to the attractive
forces of unlike surfaces. Consequently, the average size of
the nanoparticles increases. The adsorption of molecules with
a particular polarity on the surface of pre-existing nano-
particles with oppositely charged surfaces creates electric
double layers (EDLs), which neutralizes the nanoparticles.
Consequently, further growth of nanoparticles stops and res-
ults in the formation of nanoparticles with small average sizes
[13]. Ablation of an aluminum target in chloroform, which is
a strong polar liquid, leads to the formation of small Al nano-
particles. Additionally, nanostructures were also observed on
an aluminum target, where the ablation occurs. The interac-
tion of the liquid vapour with the metallic melt layer results in
Rayleigh-Taylor or Kelvin–Helmholtz instabilities, and con-
sequently results in the redistribution of molten layer form-
ing mushroom- or dome-like structures on the ablated sur-
faces [14−15]. The dynamics of ablation and its outcomes as
a function of laser parameters were extensively studied by
Barcikowski et al. [16].

Laser exposure on an aluminum target leads to morpho-
logical modifications such as ripples [17−22] and conical
structures. Aluminum metal exhibits a significant value of
electron–phonon coupling coefficient (γ) that facilitates the
formation of ripple/grating structures. The gratings formed
on the aluminum targets can be described as laser induced
periodic surface structures (LIPSSs). LIPSS is classified as
high spatial frequency LIPSS (HSF-LIPSS) when the grating
period (Λ) is less than the wavelength of light utilized for
the ablation. A few researchers have documented [23−26] the
ablation of Al in different liquid media but there are few
works describing the effect of liquid polarity on the products
of the ablation.

Laser induced periodic surfaces have very exciting ele-
ments that can be produced by laser ablation in liquids. Plas-
monic nanomaterials, such as silver, gold, and copper spher-
ical nanoparticles or nanostructures, have broad applications.
Apart from the mentioned plasmonic nanomaterials, aluminum
nanomaterials are equally exciting due to their unique optical
properties. Aluminum is an economic metal with a very
low melting temperature of 660°C, compared to other plas-
mic metals. Aluminum nanomaterials have tremendous
applications in defense science. In particular, Aluminum nan-
omaterials can be utilized as additives in propellants and pyro
techniques [27] since aluminum nanoparticles release a signi-
ficant amount of heat during their exothermal oxidation. To
achieve significant heat release from aluminum nanopar-
icles, pure aluminum nanoparticles need to be synthes-
ized without oxidation which is a tedious task since alu-
mium can be easily oxidized. The detonation velocity and
burn rate of an explosive decreases rapidly because the alu-
mium nanoparticles added to it are oxidized. To achieve the
non-oxidized aluminum nanoparticles, we attempted laser
ablation in oxygen-free organic liquids, such as chloroform,
which significantly diminishes the instant oxidation of alu-
mium nanoparticles at the time of their generation. After
synthesizing the aluminum nanoparticles, colloids were pre-
served in air tight bottles to prevent the further oxidation due
to environmental oxygen. The main advantage of laser abla-
tion of Al target in polar liquids, such as chloroform, is the
formation of EDLs on the surface of primary aluminum nano-
particles. Thus, formed EDLs neutralize the further growth
and hence aluminum nanoparticles with smaller size can be
synthesized.

2. Experimental

Laser ablation of aluminum targets immersed in chloro-
form were performed using a Ti:Sapphire laser system,
which delivers nearly transform limited laser pulses of ~2 ps
(repetition rate of 1 kHz, central wavelength of 800 nm). An
aluminum target was submerged in a chloroform (CHCl₃)
liquid layer (2−3 mm above the target surface) such that the Al
target was exactly parallel to the surface of the optical bench.
An aspherical convex lens of focal length (~8 cm) was used
to focus the laser beam on the target surface. It is diffi-
cult to focus the laser light beam exactly on the Al target sur-
face immersed in the chloroform due to the refractive index
of the medium that displaces the focal plane. This displace-
ment of the focus results in a poor rate of ablation and, con-
sequently, lower yields of nanoparticles. To avoid this, the
focal plane of the laser beam was adjusted by displacing the
target or lens. The estimated beam waist (ω₀) at the focus in
air was estimated to be ~15 μm. The petri dish comprising
chloroform with an immersed Al target was placed on a mo-
torized X–Y stage, which can be operated through the mo-
tion controller. The utilized energy per pulse was estimated
as ~350 μJ. Two motorized linear stages (X and Y) mediate
by a motion controller (Newport ESP 300) to change the
speeds to 0.2 and 0.4 mm/s, respectively. Both of the motor-
ized stages operated in such a way to draw parallel lines on
the Al sample, at a separation of ~150 μm. The time of the
laser irradiation was ~5 min and each scan gives 20 periodic
lines on the aluminum target. Complete details of the exper-
imental arrangement of ultrafast laser ablation of metal tar-
gets in liquid can be seen in our earlier work [28]. While ad-
justing the focal plane of the lens on the surface of the target,
one has to ensure the process of ablation by looking at the
visible plasma generated at the point of laser irradiation. Ad-
ditionally, a cracking sound made by the laser irradiation during laser ablation is another confirmation that the focus is on the surface of the target. Post ablation, laser exposed Al targets were removed from the liquids and preserved after a careful cleaning. Immediately after ablation, aluminum colloidal solutions were characterized by UV−Vis spectrometer and energy dispersive spectrometer (EDS, OX-Ford Instruments), and laser exposed portions were investigated by a field emission scanning electron microscope instrument (FESEM, Ultra 55 from Carl ZEISS). UV−Vis spectra confirmed the presence of Al NPs by the localized surface plasmon resonance (LSPR) peak. In this work, we fabricated Al nanoparticles in chloroform and simultaneously achieved HSF-LIPSSs at an optimum laser energy of ~350 μJ. In addition to fine ripples, a coarse grating of a period of 700 nm, which is near the incident wavelength (800 nm) was achieved.

3. Results and discussion

3.1. Spherical and non-spherical Al nanoparticles

 Aluminum colloids prepared by the laser ablation of Al targets in chloroform with ~2 ps pulses are preserved in an air tight bottle to avoid light exposure. Prior to ablation, pure chloroform did not show any coloration but Al colloids in chloroform exhibited a golden yellow coloration, which is a confirmation for the formation of aluminum nanoparticles in the chloroform. The coloration was attributed to the LSPR of Al colloids. Al colloids were characterized by UV−Vis absorption spectrometer and the localized surface plasmon peak was ~324 nm. The localized surface plasmon peaks of Al colloids in different organic solvents were demonstrated to be very weak plasmon peaks but in the case of Al NPs in chloroform it was a broad peak whose shoulder was extended to the visible region with a plasmon bandwidth (FWHM) of ~70 nm, as shown in Fig. 1. Though the surface plasmon resonance peak position was in the UV region, coloration of the colloidal solution was golden yellow due to the extension of the shoulder of the recorded UV−Vis spectrum into the visible region. The plasmon bandwidth also demonstrates the formation of Al nanoparticles with different sizes.

![Fig. 1. UV−Vis absorption spectrum of aluminum nanoparticles fabricated at ~350 μJ in chloroform exhibiting a LSPR peak at ~324 nm.](image1)

FESEM characterization was carried out to find the morphology of the aluminum nanoparticles fabricated in chloroform. The FESEM data obtained from the aluminum colloidal solutions demonstrated that most of the synthesized aluminum nanoparticles were spherical in nature. The FESEM image also demonstrated well mono-dispersed aluminum nanoparticles with larger and smaller sizes. As the profile of the laser beam utilized for ablation is Gaussian, the trend of ablation occurred at the center of the laser beam is not the same as the ablation performed at the shoulders of the laser beam. Consequently, the products of ablation are also different as observed in Fig. 2.

![Fig. 2. FESEM image of aluminum nanoparticles in chloroform, which demonstrates the spherical nature of aluminum nanoparticles. The inset shows the histogram of Al NPs whose average size was (27 ± 3.6) nm.](image2)
Fig. 2 depicts the FESEM image of Al NPs on a carbon strip. To estimate the average size, four FESEM images recorded at various locations on the carbon tape were considered. The histogram was constructed by considering the estimated sizes as a whole and the estimated average size obtained using ImageJ software was $(27 \pm 3.6)$ nm. In addition to the spherical nanoparticles, there were also triangular, pentagonal, and hexagonal aluminum nanoparticles synthesized in chloroform. The aluminum nanoparticles with different shapes are active elements for tuning the LSPR peaks from UV regions to near IR and have many plasmonic applications. However, in this work, their density was low, and hence they could not significantly modify/influence the UV−Vis absorption peak (Fig. 1). Fig. 3 illustrates the synthesized aluminum nanoparticles with different morphologies. We could count the number of the triangular/pentagonal/hexagonal aluminum nanoparticles with extreme care and found that the ratio of spherical to other morphologies is 50:1.

When a metal target immersed in a liquid medium is irradiated by a focused ultrafast laser pulse, local melting occurs and a metallic plume is generated on the target surface. The plume comprises atoms, molecules, ions, atomic clusters, and other constituents. The liquid layer adjacent to the plume gets evaporated and exerts a recoil pressure on the metal plume. As this recoil pressure is balanced by the surface tension forces in the metallic melt, the produced particles are predominantly spherical in nature.

Recently, Zhang et al. [29] reviewed ultrafast laser ablation and the inherent mechanisms involved in the formation of nanoparticles with different morphologies. Laser ablation in liquids follows three stages: first, plasma stage; second, vapor (or cavitation bubble) stage; third, interaction of nanoparticles with the molecules of the surrounding liquid medium after the collapse of the CB. Immediately after the laser irradiation beyond a threshold intensity ($10^9$ W/cm$^2$), plasma is generated on the target surface. During the expansion of the plasma, a CB will be created. The CB is a cavity formed by the shock wave, which was produced by the metallic plume during its expansion. The CB dynamics may determine the morphologies of the synthesized nanoparticles. During the process of ablation, a CB formed and the properties of the bubble, such as volume, expansion velocity, and life time, influenced the nucleation, growth mechanism, and hence the final morphologies of the nanomaterials [30–31]. The morphologies of the particles synthesized depend on the pressure and temperature inside the CB. The pressure inside the CB is determined by the liquid parameters such as the polarity and viscosity. In the laser ablation, the formed CB comprises metal condensates along with the liquid vapor. Consequently, these complicated interactions influence the morphologies of the synthesized nanoparticles. The formation of nanomaterials with different sizes and morphologies can be described as the outcomes of oscillations and collapse of the CB, which explained by Raleigh–Plesset (RP) equation [32] as shown in Eq. (1):

$$R d^2R/dt^2 + \frac{3}{2} \left( \frac{dR}{dt} \right)^2 = \frac{1}{\rho} \left[ \left( p_0 - p_v + \frac{2\sigma}{R_0} \right) \left( \frac{R_0}{R} \right)^3 - p_0 + p_v - \frac{2\sigma}{R_0} - \frac{3\gamma R_0}{R} \right]$$

where $R_0$ is the initial CB radius, $R$ is the time (delay time, $t$) dependent bubble radius after the irradiation of the laser pulse, $\rho$ is the density of liquid, $p_0$ is the hydrostatic pressure, $p_v$ is the pressure inside the bubble, $\sigma$ and $\eta$ are the surface tension and the viscosity of liquid, and $\gamma$ is the polytropic constant. The solution of the above equation describes the complete characteristics of the synthesized nanomaterials on the basis of CB dynamics.
On the other hand, ablation of aluminum targets immersed in polar organic liquid chloroform was performed with ~2 ps laser pulses. A pulse is ultrashort when its pulse duration is shorter than the electronic response/relation time of materials (~1 ps). Thus, the 2 ps pulses used in the present experiment are considered to be nearly ultrashort pulses. Ultrafast laser ablation of metals in liquid media is a well-known method to synthesize nanoparticles. The majority of reports say that the nature of the synthesized nanoparticles is spherical. However, in this study, we found the traces of non-spherical nanoparticles. As the pulse duration is short, the complicated laser−matter interaction underneath the liquid medium may lead to the formation of non-spherical nanoparticles. Many researchers reported the formation of spherical nanoparticles in ultrafast laser ablation but few reported the formation of such triangular or hexagonal nanoparticles. Consequently, we do not have a very clear understanding of the theoretical base of these structures and further studies are still needed.

3.2. LIPSS of aluminum

In addition to the Al colloids of spherical and non-spherical morphologies, laser exposed portions of aluminum also exhibited mushroom type structures, because Rayleigh instabilities occurred due to the strong interaction of the plasma plume with the surrounding liquid medium. FESEM analysis of the laser exposed Al targets ablated in CHCl$_3$ demonstrated the LIPSSs. Fig. 4 illustrates the FESEM image of ripple structures formed on the ablated Al metal target.

Depending on the grating period ($\Lambda$), these surface structures are HSF-LIPSSs (grating period much less than the incident wavelength) and low spatial frequency LIPSSs (LSF-LIPSSs) (grating period comparable to the incident wavelength). The LSF-LIPSSs are considered coarse ripples and HSF-LIPSSs are fine ripples [33]. FESEM image of the laser exposed aluminum target demonstrated the presence of coarse ripples and fine ripples. These coarse and fine ripples were not formed individually but mixed with each other. The grating period of the coarse structures was ~700 nm and that of the fine structures was ~280 nm as evident from Fig. 4. The coarse grating (LSF-LIPSS) was perpendicular to the polarization of the incident beam whereas fine grating was parallel to the input beam polarization. Exact dynamics that evoke the periodicity of the surface structures is not yet understood. Though many theories have discussed the formation of ripples on different materials, such as semiconductors, metals, and dielectrics, the origin of the formation is still a longstanding puzzle.

Fig. 4. FESEM image of laser induced periodic surface structures obtained on an aluminum target surface when ablated in CHCl$_3$ with ~2 ps laser pulses (inset shows the magnified view of coarse ripples).

According to the references [34−35], these ripples may be due to the interference of the electric field of the incident laser beam or the incident wave with the surface scattering electromagnetic wave caused by the roughness of the sample. This interference modulates the periodic electric field on the surface and results in the formation of LIPSS. Formation of gratings near the scratch indicates that the surface roughness is the primary reason for the broken symmetry and leads to the formation of grating. They also described the formation of the damaged structures using electromagnetic theory, according to which, periodic damage patterns are the result of inhomogeneous absorption of laser energy beneath the sur-
face. These are mediated by the intrinsic surface roughness of the metal. Temple and Soileau [36] demonstrated that the non-radiative, short range fields associated with the surface defects of the materials might cause the surface scattered waves. Huang et al. [37] described the formation of the grating structure on the basis of propagating surface plasmon (PSP) and the excitation by the incident laser pulse. Reif et al. [38] had an alternative mechanism of grating formation in which the self-organized structures are due to the non-stable metallic plume formed over the course of ablation. In this process, the direction of the input laser electric field acts as a driving force in the formation of self-organized surface structures under the influence of an ultrashort pulse. Another reason behind the formation of the grating structure may be the complex refractive index of laser exposed portions of the target on which irradiation is performed. Due to the impact of laser pulses, the effective number of charged carriers (mostly electrons) generated at the site of laser impact dramatically modifies the complex refractive index of the material locally. This localized refractive index variations cause ripple structures. In addition to the complex refractive index, polarization of the incident field is another parameter that influences the orientation of the ripple pattern. Thus, the fabrication of ripples and their periodicity depend on the polarization of the input beam, angles of incidence, and the speed of scanning.

Coarse ripples can be observed at higher intensities due to central portion of the laser focal spot [39–40] and fine ripples might due to the complex refractive index of the modified surface. The period of the grating [41] is given by Eq. (2):

$$\Lambda = \frac{\lambda}{1 \pm \sin \theta}$$  

(2)

where $\theta$ is the angle of incidence and $0^\circ$ for normal incidence. Thus, for metals, the periodicity almost equals the wavelength ($\lambda$) of the light utilized. Compared to silver and gold, the probability of the ripple formation on the aluminum targets is pretty large due to its large electron–phonon coupling constants. Experimental verification of the mentioned concept is under progress.

When a photon is incident to a metallic surface, PSPs will be generated whose wave vector is represented by $K$(surface plasmon). Metallic LIPSS supports the excitation of PSP wherein the grating period plays a crucial role in momentum conservation of the incident photon as mentioned in the following equation,

$$K_{\text{parallel}}(\text{photon}) = K_{\text{parallel}}(\text{surface plasmon}) + \frac{2\pi n}{\Lambda}$$  

(3)

where $K_{\text{parallel}}(\text{photon})$ and $K_{\text{parallel}}(\text{surface plasmon})$ are the parallel momentum components of an incident photon and the surface plasmon, respectively. When $K_{\text{parallel}}(\text{photon})$ equals to $K_{\text{parallel}}(\text{surface plasmon})$, or the metal surface is patterned to get an appropriate grating period ($\Lambda$), Eq. (3) will be satisfied, and then the incident energy will be coupled to a great extent to the target surface. LIPSS has many such applications by which the light energy can be coupled to design solar cells, waveguides, and drug delivery systems.

4. Conclusion

In summary, aluminum targets were ablated using ~2 ps laser pulses at an energy of ~350 $\mu$J in chloroform, and spherical aluminum nanoparticles with an average size of ~27 nm, as well as triangular, pentagonal, hexagonal aluminum nanomaterials were synthesized. The origin of the formation of triangular/pentagonal aluminum nanomaterials is still unclear but may be due to the dynamics of the CB determining sizes and morphologies of the ablation products. In addition to the mentioned aluminum colloids, aluminum nanostructures were also formed on the laser exposed portions on the targets. Both fine and coarse ripples whose separations were ~280 and 700 nm, respectively. The coarse ripples are known as low spatial frequency laser induced periodic surface structures and the fine ripples are known as high spatial frequency laser induced periodic surface structures. The polarity of the chloroform molecules stopped the further growth of aluminum nanoparticles by the formation of EDLs.

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