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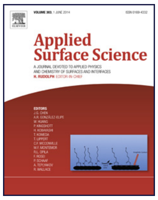

Effect of oblique incidence on silver nanomaterials fabricated in water via ultrafast laser ablation for photonics and explosives detection

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ABSTRACT

Picosecond (ps) laser ablation of silver (Ag) substrate submerged in double distilled water was performed at 800 nm for different angles of incidence of 5°, 15°, 30° and 45°. Prepared colloidal solutions were characterized through transmission electron microscopy, UV absorption spectroscopy to explore their morphologies and surface plasmon resonance (SPR) properties. Third order nonlinear optical (NLO) characterization of colloids was performed using degenerate four wave mixing (DFWM) technique with $\sim$40 fs laser pulses at 800 nm and the NLO coefficients were obtained. Detailed analysis of the data obtained from colloidal solutions suggested that superior results in terms of yield, sizes of the NPs, SPR peak position were achieved for ablation performed at 30° incident angle. Surface enhanced Raman spectra (SERS) of Rhodamine 6G from nanostructured substrates were investigated using excitation wavelengths of 532 and 785 nm. In both the cases substrates prepared at 30° incident angle exhibited superior enhancement in the Raman signatures with a best enhancement factor achieved being $>10^8$. SERS of an explosive molecule 5-amino, 3-nitro, -1H-1,2,4-nitrozole (ANTA) was also demonstrated from these nanostructured substrates. Multiple usage of Ag nanostructures for SERS studies revealed that structures prepared at 30° incident angle provided superior performance amongst all.

1. Introduction

Versatility and extreme simplicity are significant features of top-down process of pulsed laser ablation of bulk silver targets submerged in liquids (PLAL) [1–15]. The technique facilitates fabrication of impurity free Ag nanoparticles (NPs) and well textured Ag metallic nanostructures (NSs) in a short time without contamination of the environment since rupture of the metal target takes place underneath the liquid layer. Simultaneous fabrication of the NPs and NSs in a single step is not possible with most of the other established lithographic methods. Moreover, products of PLAL (NSs and NPs) need not be treated using separate chemicals since the method itself is green and free from precursors or surfactants akin to other techniques [16,17]. Aforesaid salient features of PLAL technique renders it to play a crucial role in plasmonics, photonics, and biosciences. Wide range applications of plasmonic (Ag) NPs include anti-bacterial [18,19] agents, cancer cell destroyers [20,21], elements in device making of optical limiters and essential building blocks of solar cell fabrication etc. [22,23]. Similarly, Ag nanostructured surfaces play a decisive role in surface enhanced Raman scattering spectroscopy (SERS) [24–30] for trace detection of adsorbed molecules, including potential explosives [31].

In PLAL, a focused pulsed laser beam is allowed to fall on a metallic target submerged in liquid, leading to absorption of the laser pulse energy through the conduction electrons of metal target via inverse Bremsstrahlung. Consequently, ejected ballistic electron gas attains higher temperatures than the surrounding lattice which remain cold. After a few ps [32,33] electron gas at higher temperature transfers heat energy to lattice through electron-phonon coupling achieving a state of equilibrium. Gradient of temperatures of ballistic electron gas, lattice system and the dynamics of equilibrium are successfully explained by a two-temperature model [34]. Post equilibration, if the temperature attained by entire system is greater than melting point of metal target then portion of metal at which laser energy is deposited turns to melt phase. The metallic melt acts as a reservoir for fabrication of NPs and NSs. A complicated laser-matter interaction under the liquid layer leads to the

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generation of plasma plume at the point where the local melting has taken place. Later, the plasma expands into surrounding liquid medium resulting in generation of a shockwave. During the process of expansion, plasma plume cools down and transfers the energy to liquid medium. Consequently, cavitation bubble [35] is generated in the liquid medium which further expands. After a certain period (typically a few hundred microseconds) where inside pressure decreases compared to the surrounding liquid medium, cavitation bubble collapses followed by generation of a second shock wave [36]. In fact, the exact stage at which nanomaterials are fabricated is still being debated. Some groups, through extensive experimental research and modeling, have suggested that the nanomaterials are generated during the expansion of cavitation bubble inside it on a time scale of the order 10^{-6}–10^{-4} s [37,38]. The expansion of cavitation bubble into liquid medium exerts a recoil pressure on the metallic melt formed under plasma plume. Recoil pressure splashes the melt and residual recoil pressure redistributes the metallic melt. Former process guides the fabrication of nanoparticles and latter leads to the fabrication of nanostructures. Nanoentities inside the cavitation bubble are at a higher temperature than liquid environment. Ag nano-materials exhibit fascinating electronic, optical, and other physical properties depending on their crystallinity, composition, shape, and size. Furthermore, Ag NPs support strong localization of surface plasmon resonances (LSPR) [39–41] than the other well known plasmonic metals. Besides, Ag colloids and nanostructured Ag targets (with grating formation along with the presence of Ag nanoparticle grains) act as an efficient SERS active platform through the excitation of propagating surface plasmons (surface plasmon polaritons) and non-propagating surface plasmons (localized surface plasmons) [42,43].

Size and shape of the fabricated metallic nanomaterials in PLAL not only depend on laser parameters [44–48] such as wavelength, pulse duration, energy per pulse, repetition rate, beam waist at the focus, number of laser pulses per spot but also on the nature of surrounding liquid. Extensive studies of laser ablation in liquids investigating some of these parameters and resulting applications of the generated NPs have been performed by Meunier group [49–53]. Amendola et al. [36] carried out an extensive study of PLAL through formation of cavitation bubble and provided a panoramic view of how the various laser parameters and the nature of liquid influenced ablation in a qualitative manner. However, very few articles extensively dealt with detailed dynamics of laser ablation in liquid and dependence of products on laser parameters [54–56]. Notwithstanding several works reporting fabrication of Ag nanomaterials (both NPs and NSs) through pulsed laser ablation in liquids, effect of nonzero angle of incidence has not yet been attempted/reported. Earlier reports have demonstrated the effect of lateral beam waist on ablation but not the axial beam waist which is also the part of ablation when the angle of incidence is changed. Ganeev and Jia [57] investigated surface modifications of silicon through laser ablation with fs pulses at an angle of incidence close to Brewster angle using interferometry and studied the dependence of grating period on the angle of incidence. Sing and Tripathi [58] dealt the laser beat wave excitation of surface plasma wave at an oblique incidence of laser beams through which beams exerted a ponder motive force on free electrons at the frequency of beat, consequently producing a nonlinear current that drives plasma wave resonantly. The surface plasma wave causes an efficient heating of electron system which leads to ablation of material and thus the dependence of ablation on angle of incident laser beam was retrieved theoretically. George et al. [59] reported the angular dependence of focused ns laser pulses on to polymer films at moderate energies revealing the control of complex nanostructure formation at oblique incidences.

In our earlier works, fabrication and effects of polarity of liquid medium was investigated through ablation studies of Al targets in polar and non-polar liquid media [15]. The effects of over writing (multiple/double/single line ablation) of Ag/Cu substrates in different liquid media were also investigated along with the Raman activity of fabricated NSs/NPs [46,60]. In continuation of our earlier work, dependence of non-zero angle of incidence on ablation of Ag substrate in double distilled water is investigated in the present work. Most of the earlier studies of ablation at non-zero angle of laser incidence were carried out in ambient air and that too for non-metals. In the present work we attempted to (a) fabricate the Ag nanomaterials for 5°, 15°, 30° and 45° angle of laser incidence on the target surface (experiments were also repeated for constant fluence on the target surface at these four angles of incidence) (b) investigate the specific angle of incidence at which superior products were achieved after ablation (c) characterize the nonlinear optical (NLO) properties of the prepared Ag colloids using fs degenerate four wave mixing (fs-DFWM) at 800 nm in the BOXCARS geometry (d) investigate surface enhanced Raman activity of Ag substrates fabricated at different angles of incidence with Rhodamine 6G (μM concentration) in methanol excited with 532 nm and 785 nm (d) record the Raman spectra of high explosive molecule of 5-amino-3-nitro-1H-1,2,4-triazole (ANTA) at mM and μM concentrations. In this communication we also report the multiple utility of Ag NSs when combined with appropriate cleaning methods.

2. Experimental details

Complete details of the experimental setup are presented in our earlier works [15,46]. Briefly, Ag substrate submerged in double distilled water in a Pyrex cell and was positioned on a motorized *X*–*Y* stage. In our earlier fabrication experiments (of Ag NPs) achieved through double line ablation, thickness of liquid layer used was ~2–3 mm whereas in the present case liquid level was maintained at ~5 mm so as to accommodate the angle dependent ablation. Initially plane polarized (P-polarization) laser pulses were allowed to focus vertically onto the Ag substrate through a plano-convex lens of focal length 25 cm. Optimization near focus was carried out by observing intense plasma plume and cracking sound when focused laser beam impinged on the metallic target [61,62]. Angle of incidence was altered by tilting the mirror which was directing focused laser beam onto target surface. The angle of incidence was adjusted and confirmed by a protractor whose center was placed at the position of visible plasma plume. The schematic of non-zero angle of laser incidence carried out on Ag substrate is illustrated in Fig. 1(a). *X*–*Y* translation stages, interfaced to Newport ESP 300 motion controller, were utilized to draw periodic line structures on the Ag substrate with separations of ~20 μm. Fig. 1(b) illustrates the schematic of single line and multiple line ablation mechanisms. The scanning speeds of the *X*–*Y* stages were ~0.1 and ~0.4 mm/s. The uncertainty in adjusting focus exactly on the metal substrate because of displacement caused by refractive index of surrounding liquid and other nonlinear optical effects was taken care of by observing the plasma [63]. The theoretical lateral beam waist (ω_{lateral}) estimated at focus (in air) was ~10 μm while the theoretical axial beam waist (ω_{axial}) was ~20 μm. However, in reality beam waist at focus on the target surface immersed in water will not be the same as in air. Estimated beam waist at focus is nearly double that of the waist in air. Barcikowski et al. [64] explained the width of line structure can be approximated to $2\omega_0$ when the ablation is carried out by ultrafast laser pulses. For exact beam waist estimation, craters were made on Ag target immersed in double distilled water (5 mm above target surface) to estimate the degree of stretch and depth. Accordingly, axial beam waist (ω_0) in the present experiment was estimated to be ~40 μm, based on the diameters of craters created with 90,000 pulses (exposure time of 90 s at normal incidence). For each tilting angle effective liquid layer thickness was