

Pulsed nanosecond laser ablation of gold in deionized water and aqueous chitosan solution

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ABSTRACT

Gold nanoparticles (AuNP) are produced using a Nd:YAG laser in deionized water and aqueous chitosan solutions via 1064 nm nanosecond laser ablation and subsequent 532 nm nanosecond laser irradiation. AuNP produced in deionized water under single laser ablation and subsequent irradiation for 20–40 min exhibited coalescence and the formation of nano-chains, with average particle diameters ranging from 34.3 to 18.8 nm and 37.2 to 27.3 nm, respectively. The introduction of chitosan as a bio-compatible surfactant yielded lesser average diameters and tighter size-distributions with a narrow range of UV-Vis absorption spectra values (514–525 nm). For instance, at 20 and 40 min, the single laser ablation and subsequent irradiation produced the average diameters of 12.3 and 5.3 nm and 5.7 and 4.3 nm, respectively. Increases in ablation and irradiation time decrease AuNP size. As time increased, the size-distributions of the AuNP produced in chitosan solution narrowed and the particle size monotonically decreased. Chitosan functionalized the AuNP surface, promoting hydrophobicity, preventing electrostatic attraction of the Au nanoparticles, thus inhibiting coalescence and agglomeration. UV-Vis absorption spectra, TEM and HR-TEM images are used to verify AuNP size distributions. X-ray diffraction measurements of AuNP produced in chitosan confirmed crystallite size and the absence of gold-oxide despite the high-energy laser ablation. Furthermore, samples prepared in chitosan solution showed minimal agglomeration after 24 months.

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1. Introduction

The uses of gold nanoparticles (AuNP) range from catalysts [1,2], nanolenses [3] to biosensors [4–6]. For catalysis applications, the catalytic activity of AuNP increases as the particle size decreases [6]. Within the biomedical field, selective size and shape AuNP can be used as high-resolution biosensors for cancerous tissues and also as photothermal therapy for cancerous cells [7]. Additionally, size-dependent surface plasmon properties of AuNP allow for greater optical absorption in photovoltaics leading to greater photocurrents [8]. Thus, the size control and the subsequent stability of AuNP produced by means of chemical precipitation, pulsed laser deposition and laser ablation prove imperative for the various aforementioned applications. Laser ablation of AuNP in deionized water proves problematic due to agglomeration and coalescence, and much work has been done with the use of surfactants to produce stable sub-10 nm AuNP, which are the most

desirable for these applications. We are therefore motivated to find a means of producing free, selective sized AuNP with diameters less than 10 nm.

Nanosecond laser ablation relies on plasma-heating of the target material surface, which causes vaporization and expulsion [9] and removal [10] of molten material. Mafuné et al. [11–13] have pursued the production of AuNP in organic, anionic sodium dodecyl sulfate via laser ablation and laser-induced size control. Laser-induced size control, or irradiation, exploits the strong surface plasmon absorption of AuNP around 532 nm, which causes photofragmentation.

Amendola et al. [14] used the polar protic solvents dimethyl-sulfoxide, tetrahydrofuran and acetonitrile as water-soluble surfactants to produce stable, free AuNP under nanosecond single (1064 nm) and dual (532 nm) laser ablation and irradiation with radii less than 10 nm. Additionally, they found AuNP produced in toluene, a benzene derivative, have predominantly sub-1 nm radii due to encasement of a graphitic carbon matrix around the AuNP, presumably induced by the pyrolysis of benzene [15].

Compagnini et al. [16] prepared AuNPs in non-aqueous alkanes and thiol-alkane solutions via a 532 nm Nd:YAG laser operating with a 5 ns pulse duration and reported a reduced size distribution, attributed to S–Au bond formation and an organic alkyl shell that

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prevents agglomeration. They extended their research to *n*-alkane solutions and reported the production of sub-5 nm particles with low fluences (200 J/cm^2) and the ability to control the aspect ratio by adjusting the molecular mass of the alkane [17].

Tarasenko et al. [18] performed studies on the nanosecond ablation of gold in water via a 532 nm Nd:YAG laser and additional 266 nm laser irradiation. Their results indicated sub-10 nm AuNP with size distributions and sphericity controlled by laser fluence and wavelength and subsequent post-ablation irradiation.

Femtosecond laser ablation has the capacity to ablate materials using fluences less than those required for laser-induced explosive boiling [19], allowing for the generation of small nanoparticles without the use of a stabilizing agent. Besner et al. [20] used a two-step femtosecond laser ablation process to produce sub-10 nm colloidal AuNP with narrow size distributions in a neutral aqueous environment.

Kabashin and Meunier [21] curtailed the size and dispersion of colloidal AuNP prepared in deionized water by femtosecond laser ablation via fluence. They showed that low-fluence ablation yields mono-dispersed AuNP colloids with small sizes $\approx 3\text{--}10 \text{ nm}$ due to the absence of heating, whereas high-fluence ablation introduces plasma heating, which produces large particles with larger size distribution, regardless of ablation time. Furthermore, they used cyclodextrins to yield AuNP with mean diameters less than 4 nm [22]. Sylvestre et al. [23] used cyclodextrins in femtosecond laser ablation to generate AuNP on the size of 2–2.5 nm, and the cyclodextrin prevented aggregation after 24 months of storage. Additionally, they controlled and reduced the size of AuNP produced by femtosecond ablation to sub 10 nm by increasing their electrostatic repulsion through the addition of KCl, NaCl and NaOH [24].

In this work, we propose the use of chitosan as a biocompatible water-soluble surfactant for surface functionalization and size control of AuNP generated via nanosecond laser ablation. Chitin is an abundant, naturally occurring mucopolysaccharide, consisting of β linkages which exhibits minimal immunogenicity [25]. Chitosan, the *N*-deacetylation derivative of chitin, is a chelating agent, which proves useful for de-flocculation and stabilization of cationic metal ions [26]. Chitosan can possess anionic charges from the oxygen (2^-) molecule or cationic charges from the removal of acetyl ($\text{CH}_2\text{-CO}$) groups and the release of amine groups (NH), depending on the degree of deacetylation [27].

2. Experimental set-up, procedure and measurements

Fig. 1 illustrates the experimental apparatus used for laser ablation of gold in deionized water and aqueous chitosan solutions as reported [28–30]. The T-shaped quartz glass ablation cell was 125 mm long by 75 mm wide. The 50 mL of deionized water and 0.05% by weight chitosan in deionized water solutions were placed in this cell. A gold sheet, provided by Alfa Aesar (99.998% purity, $25 \text{ mm} \times 25 \text{ mm} \times 1 \text{ mm}$ thick, smooth in surface as received) was submerged in the various solutions during laser ablation roughly 12.5 mm below the waterline. Four sets of experiments were conducted: (i) single laser ablation of gold in deionized water, (ii) single laser ablation of gold in chitosan solution, (iii) laser ablation and irradiation of gold in deionized water, and (iv) laser ablation and irradiation of gold in chitosan solution.

For single laser ablation experiments, a 1064 nm Coherent JMAX43, single-mode, Q-switched neodymium-doped yttrium aluminum garnet (Nd:YAG) laser, provided by Oriel Instruments was used. This laser had a pulse duration of 5.5 ns operating at 10 Hz. Constant laser attenuation at 90.4% of maximum power produced an average laser pulse energy of 112.07 mJ, with a standard error of the mean of $\pm 0.0114\%$, as measured by an

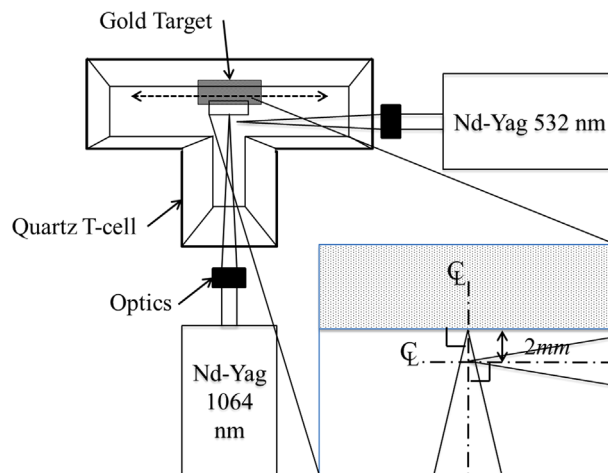


Fig. 1. Experimental set-up used for single laser ablation and secondary laser irradiation experiments.

EnergyMax 400 Laser energy meter provided by Molectron Detector, Inc. The laser beam was focused approximately 6 mm below the surface of the solutions and the gold sheet was placed 50 mm from the focal lens of the laser. To keep the focal distance constant throughout the ablation process, the gold sheet was suspended on a two-axis stage that allowed translation.

For laser ablation and irradiation experiments, in conjunction with the primary Nd:YAG laser, a secondary 532 nm Coherent JMAX43, single mode, Q-switched Nd:YAG laser was used. The secondary laser also had a pulse duration of 5.5 ns operating at 10 Hz but was on a 10 ms delay from the primary laser. The laser attenuation was 90.4% which yielded an average laser pulse energy of 56.05 mJ with a standard error of the mean of $\pm 0.0214\%$. The focal point of the secondary laser was 50 mm and was perpendicular to the path of the primary laser and offset from the primary laser spot by 2 mm.

Assuming a perfect Gaussian beam [31] the spot diameter is approximated by

$$D_s = \frac{4\lambda f}{\pi d} \quad (1)$$

where f is the focal length, λ is the wavelength of the laser and d is the beam diameter, provided at 6 mm. From Eq. (1), D_s is estimated to be 11.3 and 5.6 μm for 1064 and 532 nm lasers with fluences of 87.94 and 175.93 kJ/cm^2 at the focal point, respectively. During the four sets of experiments, compressed air was used to gently agitate the solution during ablation. Each set of experiments consisted of varying the ablation time between 20 and 40 min at 5 min intervals and three trials were conducted to confirm consistency of the data.

Colloidal dispersed-phase suspensions were collected and analyzed using UV-Vis spectroscopy and both standard and high-resolution transmission electron microscopes (TEM and HR-TEM). The UV-Vis absorbance of fresh samples was made using an OceanOptics CHEMUSB-4 UV-Vis spectrometer. The UV-Vis data was collected and analyzed using SpectraSuite software. The samples were then aged for 2 years in sealed containers under ambient, room temperature conditions. These samples were then measured using a Perkin/Elmer Lambda 35 UV-Vis spectrometer. The TEM observations were performed using Jeol JEM 200CX operating at 120 keV. The HR-TEM images were performed on a Jeol JEM 2100F microscope operating at 200 keV. The TEM images were recorded and then analyzed using ImageJ software, with sample sizes of over 500 particles used to determine the size distribution. X-ray diffraction (XRD) was conducted using a Philips PW-1810 diffractometer.

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