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Gold Nanoparticles Synthesized by Laser Ablation in Water: Optical and Structural Characterizations

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ABSTRACT

In this study we report the effect of laser energy on the size and morphology of the gold nanoparticles (GNPs) prepared in deionized water by pulsed laser ablation. The optimum conditions at which gold nanoparticles obtained with controllable average size have been reported as these parameters affected the size, distribution and absorbance spectrum . Effect of energy was studied. The laser energy was divided into three regions (low, middle and high). A noteworthy change was observed at each region, as the average size ranging from 30 nm at low energy to 60 nm at high energy.

جسيمات الذهب النانوية المحضرة بطريقة الاستئصال بالليزر في الماء: دراسة الخصائص البصرية والتركيبية

الخلاصة

تم في هذا البحث دراسة تاثير معلمات الليزر على حجم وتركيب جسيمات الذهب النانوية المحضرة بطريقة الاستئصال بالليزر في الوسط السائل (الماء منزوع الايونات)، حيث تم توضيح تغير معلمات الليزر كالطاقة على حجم وتوزيع الجسيمات وكذلك الامتصاص الطيفي لها بتغير هذا العامل. تم تقسيم طاقة الليزر الى ثلاث مناطق وهي: (المنخفضة والمتوسطة والعالية) حيث لوحظ تغير يذكر في كل منطقة من خلال تغير الحجم الجزيئي للمادة النانوية من (30 نانومتر في المنطقة المنخفضة الى 60 نانومتر في المنطقة العالية).

INTRODUCTION

Last years considerable efforts have been directed to preparation and investigation of nanostructured materials. Broadly defined, nanostructured materials are solids composed of structural elements (mostly crystallites) which characteristic size falls in the range of 1 – 100 nm [1]. They include nanocomposites, loosely aggregated nanoparticles, cluster-assembled materials, nanocrystalline thin films, metal colloids as well as semiconductor nanostructures such as quantum dots, wires and wells. Due to the reduced size of their constituent elements nanostructured materials have electronic, magnetic and chemical properties, which differ considerably from those of the corresponding bulk materials. For example, nanostructured materials have been found to exhibit increased strength and hardness, higher electrical resistivity, enhanced diffusivity,

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reduced density, etc. compared to the bulk. Hence, these materials are promising candidates for a variety of applications, which include heterogeneous catalysis, gas sensor technology, microelectronics, nonlinear optics, etc. [2-4].

More than 15 years and due to unique physicochemical characteristics of gold nanoparticles and their wide usages in different fields, the number of publications on the preparation and characterization of gold nanoparticles has extensively increased [5,6]. For example, the recently recognized behavior of gold to act as large surface-to-volume ratio of nanogold as well as its inert property have widely enhanced the application of gold nanoparticles as a catalyst in the field of organic synthesis [5]. These properties are much dependent on the particle size, shape and liquid medium. It is known that optical properties of gold nanoparticles strongly depend on the size and shape [7]. The stability of suspension depends not only on size, shape but also on liquid medium. The liquid in which nanoparticles suspend can affect the surface charge of nanoparticles. Surface charge leads to repulsive forces between nanoparticles and keeps them far from each other, which results in a high stability of suspension [8]. The absorption of laser light by metal nanoparticles gives rise to a succession of energy transformation processes. These involve the successive excitation and relaxation of the metal electrons, its interaction with the lattice, i.e. electron-phonon relaxation and the phonon-phonon thermalization. Afterwards, several thermal processes like melting or evaporation can be activated. As discussed above, in the case of nanosecond-pulsed laser light, the heat diffusion from the metal particle to the support takes place on a time scale much shorter than the pulse width. This enables a simple thermodynamic treatment of the laser induced temperature rise. [9]

The laser energy was not vaporized the material, heats it and raises their temperature, propagates via heat conduction inside the material. The temperature distribution is governed by the heat conduction equation [10]:

$$\rho C_p \frac{\partial T}{\partial t} = \nabla \cdot (K \nabla T) + (1 - R) I_0 \, \alpha \, e^{-\alpha z} \qquad \ldots (1)$$

Where

ρ, Cp, K, T: represent density, specific heat, thermal conductivity and temperature, respectively. The second term on the right hand side of equation 1 represents the source term which is the laser energy absorbed by the material at a depth z from the surface, where R is the surface reflectivity, and I_0 is the laser irradiance and α is the absorption coefficient (the imaginary part of the complex refractive index, assumed to be constant) [10, 11]

Experimental Setup

The formation of gold nanoparticles is fabricated via pulsed laser ablation of the corresponding gold metal plate (99.99%) of 3 mm thickness and its dimensions 1.5 × 1 cm^2 immersed into the liquid as shown in Fig. 1. The gold plate was thoroughly washed with ethanol and deionised water to remove organic contamination and placed at the bottom of a glass vessel filled with 2.5 ml of an aqueous solution of deionized water. The gold metal plate was kept at 1 mm below the liquid surface. Pulsed Q-Switched laser Nd:YAG type (HUAFGI), (λ = 1064 nm, pulse width of 10 ns, repeating frequency of 1

Hz, and energy from (100-650) mJ was used as showing in Fig (1). The laser beam was focused by a plano-convex lens with focal length of 5 cm. The ablation process was typically done at room temperature. The surface morphology, particle size distributions and root mean square of roughness of gold layer prepared under various conditions were analyzed using atomic force microscope (AFM).The optical absorption spectrum of the solution was measured with UV-Vis spectrophotometer.

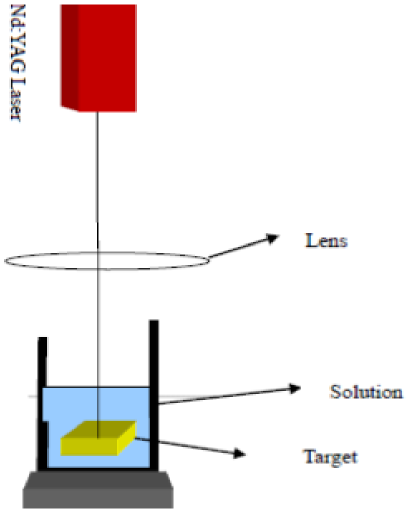


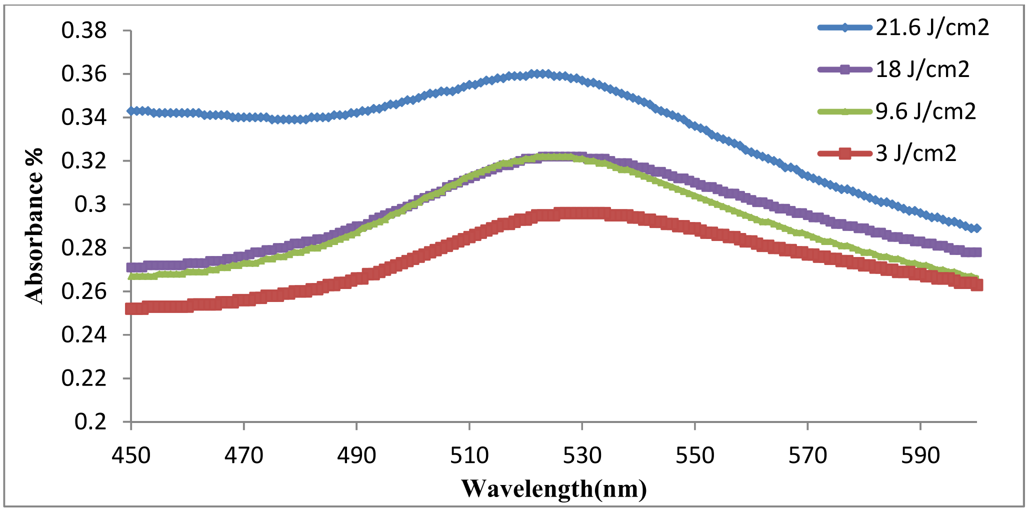
Figure (1). Schematic diagram of experimental setup

Results and Discussion

Optical properties results

Optical properties of gold nanoparticles were studied by UV-vis measurements of gold colloids.

According to the Mie theory, metal nanoparticles with spherical shape had a light absorption due to scattering of light by small particles. The optical absorption spectra of gold nanoparticles in the range of 300 - 800 nm were shown in Fig. 2. It is clearly seen that the optical properties depend much on the laser fluence. All the gold nanoparticles in different laser fluence exhibited one intense peak at about 530 nm, which assigned to the surface plasmon resonance of gold nanoparticles [12]. The maximum of optical absorption showed a red shift in the gold nanoparticles at high laser fluence. Bandwidth of optical extinction is related to the size distribution and the agglomeration of nanoparticles [13].



Figure(2). The absorbance spectrum of gold nanoparticles prepared in deionized water at laser fluence (3,9.6,18 and 21.6 J/cm^2).

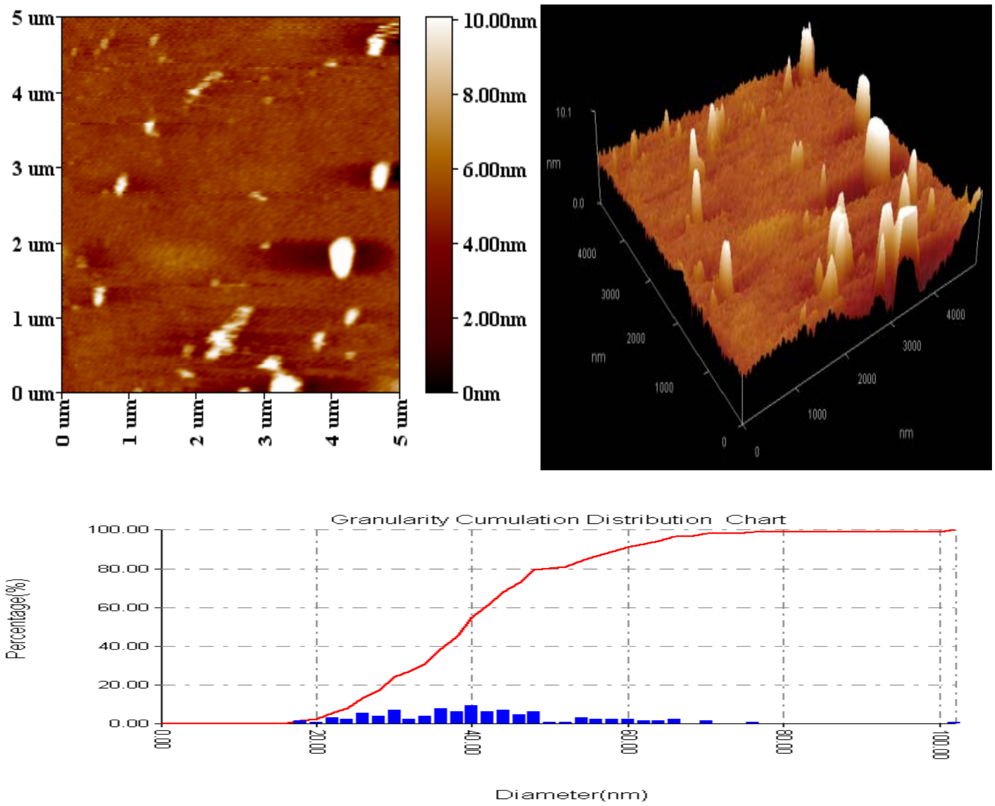
As the laser fluence increases, the height of the plasmon peak increases which indicate to the increase in the concentration of nanoparticles, till the nanoparticles reach it's critical size and the absorption coefficient of gold nanoparticles decreases and they couldn't absorb any more as they couldn't be fragment again, red shift in the Plasmon peak ensure the decrease in the average size of gold nanoparticles. As the laser fluence increases, the plasmon peak becomes narrower indicating that the particles have a homogenous distribution as the laser fluence increases.

Structural Properties

Atomic Force Microscopy (AFM)

1-At low laser fluence (Plasma Etching) (3 J/cm^2)

Under the action of the laser at low laser fluence the target is heated, but due to the strong confinement of the liquid at the surface, the vaporization rate is strongly restricted and no plume forms. In the absence of a vapor plume, the hot target is remained in contact with water promoting the oxidation of the nanoparticle oxides [14]. The reaction is initiated with the oxidation of the molten target surface by oxygen splitting of water molecules at the hot target so the hydroxide nanoparticles exist on the target surface. The gold hydroxide material on the surface then desorbs from the hot target surface and diffuses into the water and it isn't aggregated due to their negative charge so the average size of produced gold nanoparticles is small and they are produced by thermal vaporization as shown in Fig. 3



Figure(3).2D and 3D AFM images of Au NPs prepared at laser fluences3 J/cm^2

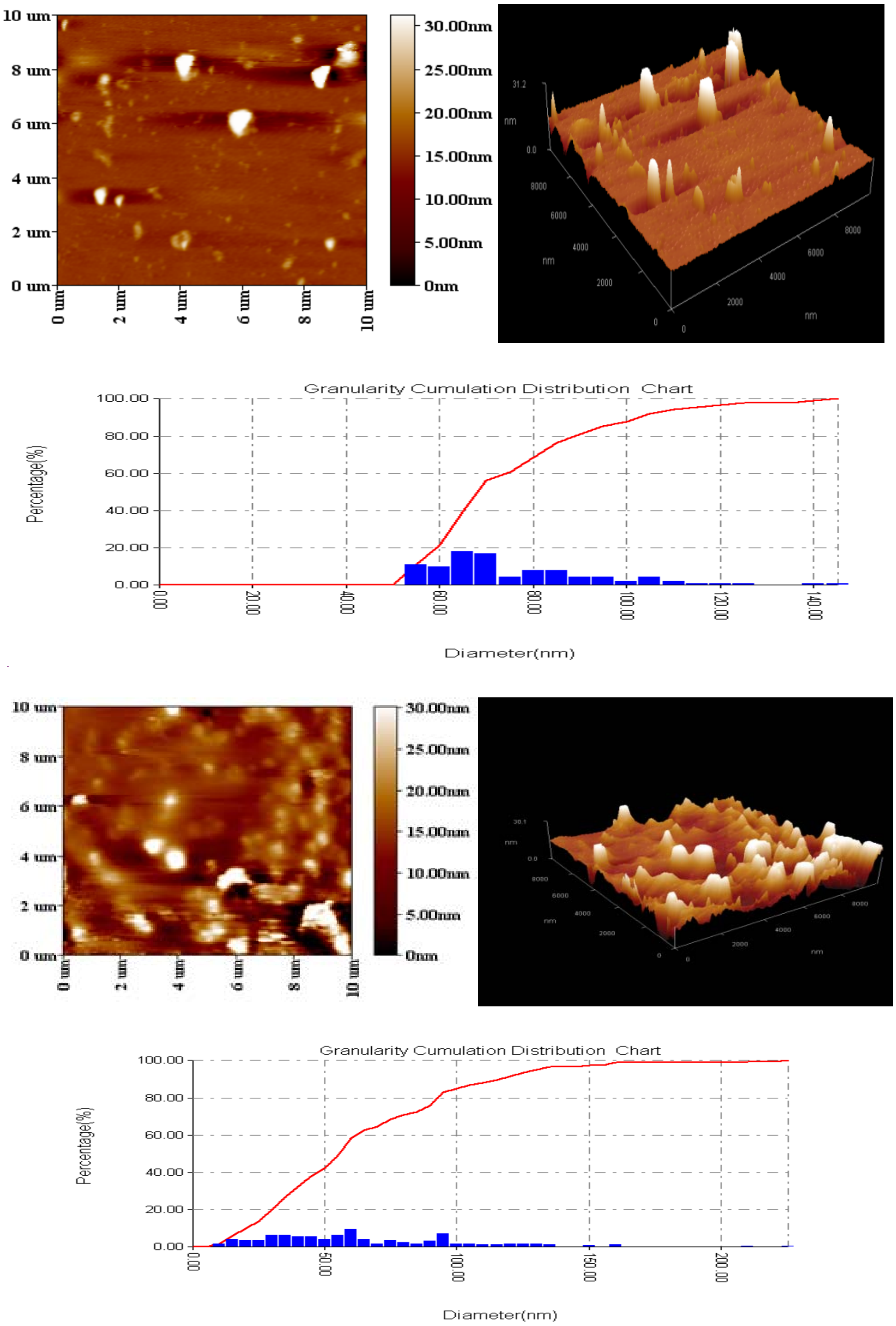
The average size is 30 nm and as it's shown the particles are small and have spherical shape and this is due to the negative charge on gold nano- particles which prevents them from aggregation and their yield is small due to presence of water at the surface of the target which restricts their growing as explained above.

Intermediate laser fluence (Plume Mixing Zone) (9.6 J/cm^2)

In this stage the plume develops more slowly and is limited to a size much smaller than in a gas atmosphere [15]. The large pressure in the confined vapor plume results in an expansion beyond the equilibrium point, the internal plume pressure equals the hydrostatic pressure of the liquid, increasing the difference between the pressure inside and outside the plume decrease the expansion until it is stopped, the hydrostatic pressure then collapse, the plume back into the target. In this region, the nanoparticles fall into two distinct size distributions those are attributed to:

1) Target surface vaporization.

2) Explosive ejection of molten droplets directly from the target, and this leads to abroad size distribution as shown in Fig. 4

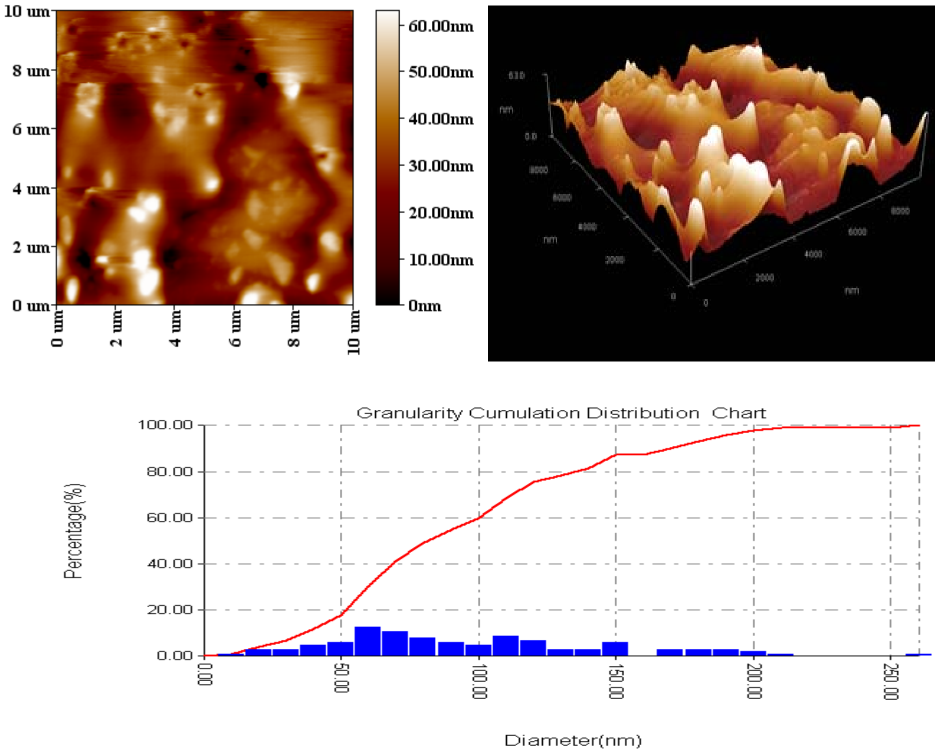


Figure(4).2D and 3D AFM images of Au NPs prepared at laser fluences9.6 J/cm^2

The surface vaporization was discussed above, the explosive ejection occurs when the temperature approaches the thermodynamics critical temperature, thermal fluctuation is amplified and the rate of homogenous bubble nucleation rises dramatically and the target makes rapid transition from superheated liquid to a mixture of vapor and equilibrium liquid droplet. At this fluence, the momentum of a plume allows it to expand further out into the liquid, increasing the plasma life time and this results in an increase of screening of laser light from surface of bulk gold target [16,17].

At High Energy of Laser Beam (Plasma Etching) (21.6 J/cm^2)

At the high laser fluence, laser energy is absorbed in the liquid to the target resulting material removal by reactive sputtering rather than direct laser ablation, as the intensity of laser in the presence of ablated material in the water, as this happen the amount of the light reaching to the target goes to zero, plasma formation in the water creates a cavitations bubble that expand and then collapse, driving highly energetic species into target [17]. In this region the average size of gold nanoparticles begins to increase again as shown in Fig.5



Figure(5).2D and 3D AFM images of Au NPs prepared at laser fluences 21.6 J/cm^2

CONCLUSION

Gold nanoparticles (GNPs) were successfully prepared by laser ablation in water. The fluence of laser beam affected on the prepared nanoparticles as the fluence increases the size of nanoparticles decreases until they reached their critical size below which the particle not sensitive to the laser fluence. As the fluence increases above this value the nanoparticles begin to agglomerate again and the size increases. The size distribution and shape can be controlled by optimizing the laser parameter such as fluence of laser beam.

REFERENCE

[1].U. Kreibig, M. Vollmer," Optical Properties of Metal Clusters", Springer, Berlin (1995).

[2]. M.S. Sibbald, G. Chumanov, T.M. Cotton, J. Phys. Chem. 45, 721 (1998).

[3].R.A.Ganeev, A.I.Ryasnyanskii, T.Usmanov, Quantum Electronics 31, 185 (2001)

[4]. J. Neddersen, G. Chumanov, T. Cotton, Appl. Spectr. 47, 1959 (1993).

[5]. F. K. Alanazi, A. A. Radwan and I. A. Alsarra, "Bio-pharmaceutical Applications of Nanogold," Saudi Pharmaceutical Journal, Vol. 18, No. 4, , pp. 179-193,2010.

[6]. E. J. Yoo, T. Li, H. G. Park and Y. K. Chang, "Size-Dependent Flocculation Behavior of Colloidal Au Nanoparticles Modified with Various Biomolecules," Ultramicroscopy, Vol. 108, No. 1, pp. 1273-1277, 2008.

[7]. K.L. Kelly, E. Coronado, L.L. Zhao and G.C. Schatz // J. Phys. Chem. B 107 (2003) 668.

[8].D. Exerowa and D. Platikanove, Colloid stability: The role of surface forces - Part1 (Wiley-VCH,Weinheim, 2007).

[9].Abdulrahman K.Ali (Preparation of Ag and Au nanoparticles by pulsed laser ablation in liquids) Doctoral Thesis, University of Technology, 2010.

[10].C. Liu (A study of particle generation during laser ablation with applications) Doctoral Thesis, University of California, Berkeley, 2005, 1-189.

[11].W. Chan, R. S. Averback, D. G. Cahill and A. Lagoutchev (Dynamics of femtosecond laser-induced melting of silver) physical review B 78 (2008) 214107.

[12]..A. Mishra, P. Tripathy, S.Ram and H.J. Fecht// Nanosci. Nanotechnol. 9 4342, 2009.

[13]. J. P. Sylvestre, S. Poulin, E. Sacher, M. Meunier and J. H. T. Luong, "Surface Chemistry of Gold Nanoparticles Produced by Laser Ablation in Aqueous Media," Journal of Physical Chemistry B, Vol. 108, No. 34, pp. 16864-16869, 2004.

[14]. B. Xu, R. G. Song, P. H. Tang, J. Wang, G. Z. Chai, Y. Z. Zhang and Z. Z. Ye, "Preparation of Ag Nanoparticles Colloid by Pulsed Laser Ablation in Distilled Water," Key Engineering Materials, Vol. 373-374, pp. 346-349, 2008.

[15]. A. Sasoh, K. Watanabe, Y. Sano and N. Mukai, "Behav-ior of Bubbles Induced by the Interaction of a Laser Pulse with a Metal Plate in Water," Applied Physics A: Material Science & Processing, Vol. 80, No. 7, pp. 1497-1500, 2005.

[16]. W. T. Nichols, T. Sasaki and Naoto Koshizaki, "Laser Ablation of a Platinum Target in Water. I. Ablation Mechanisms," *Journal of Applied Physics*, Vol. 100, No. 11, pp. 114911-114917, 2006.

[17]. W. T. Nichols, T. Sasaki and N. Koshizaki, "Laser Abla-tion of a Platinum Target in Water. III. Laser-Induced Reactions," *Journal of Applied Physics*, Vol. 100, No. 11, pp. 11-114913, 2006.