EFFECT OF THE MAGNETIC FIELD ON THE SYNTHESIS OF COLLOIDAL SILVER AND GOLD NANOPARTICLES BY LASER ABLATION IN BIDESTILATED WATER

EFECTO DEL CAMPO MAGNÉTICO EN LA SÍNTESIS DE NANOPARTÍCULAS DE ORO Y PLATA COLOIDAL POR ABLACIÓN LÁSER EN AGUA BIDESTILADA

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Abstract

The effect of the magnetic field of 0.3 T on the concentration, distribution of sizes in suspension, and zeta potential of colloidal gold and colloidal silver nanoparticles, obtained by considering the pulsed laser ablation in double distilled water was studied. The magnetic field was transverse to the direction of incidence of the laser radiation and parallel to the surface of a submerged target. An Nd: YAG laser was used (1064 nm in wavelength, 10 ns in duration, a repetition rate of 10 Hz, and 37 mJ of energy) to ablate targets. The colloids were characterized by inductively coupled plasma optical emission spectroscopy,

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ultraviolet-visible spectroscopy, dynamic light scattering, and zeta potential. Concentration analysis suggested that applying a magnetic field of 0.3 T during nanoparticle synthesis leads to higher concentration. Applying magnetic field led to an eleven percent increase in the concentration of the colloid with gold nanoparticles and a five percent increase in the concentration of the colloidal silver nanoparticles. The absorption spectra suggested the presence of spherical nanoparticles. When analyzing the effect of the magnetic field on the hydrodynamic size distribution of the nanoparticles and the zeta potential of the colloids, no significant changes were evidenced. The magnetic confinement of the plasma-induced by laser ablation caused changes in the characteristics of the colloids.

Keywords: Laser ablation in liquids, magnetic confinement, nanoparticles concentration.

Resumen

Se estudió el efecto del campo magnético (0.3 T) sobre la concentración, distribución de tamaños en suspensión y potencial zeta de nanopartículas coloidales de oro y plata, obtenidas al considerar la técnica de ablación láser pulsada en agua bidestilada. El campo magnético fue transversal a la dirección de incidencia de la radiación láser y paralelo a la superficie del blanco sumergido. Se utilizó un láser Nd:YAG, emitiendo pulsos de 1064 nm de longitud de onda, 10 ns de duración, razón de repetición de 10 Hz y 37 mJ de energía. Los coloides fueron caracterizados al considerar las técnicas: espectroscopia de emisión por plasma de acoplamiento inductivo, espectroscopia ultravioleta-visible, esparcimiento dinámico de luz y potencial zeta. Los análisis de concentración demostraron que aplicar campo magnético de 0.3 T durante la síntesis de nanopartículas conlleva a obtener mayor concentración. Aplicar campo magnético conllevó a incrementar en once por ciento la concentración del coloide con nanopartículas de oro y en cinco por ciento la concentración del coloide con nanopartículas de plata. Los espectros de absorción obtenidos son característicos de nanopartículas esféricas. Al analizar el efecto del campo magnético en la distribución de tamaños hidrodinámicos de las nanopartículas y en el potencial zeta, no se evidenció cambios significativos. El confinamiento magnético del plasma inducido por ablación láser ocasionó cambios en las características de los coloides.

Palabras clave: Ablación láser en líquidos, confinamiento magnético, concentración de nanopartículas.

Introduction

The synthesis of colloidal metallic nanoparticles by means of the pulsed laser ablation technique in liquids makes it possible to obtain ligand-free nanoparticles. The technique consists essentially of the interaction of high-power pulsed laser radiation with a submerged target. During the interaction of nanosecond-pulsed laser radiation and a submerged solid, the material is extracted from the surface of the target. The extracted material interacts with the laser pulse and results in the formation of a plasma. Plasma expansion is restricted by the low compressibility of liquids. During plasma formation and confinement, energy is transferred to the target and the liquid. The transfer of energy to the target depends on the thermal conductivity of the plasma, the plasma temperature, and the average distance of plasma from the target [1]. The transfer of energy from plasma (during cooling) to liquid results in the formation of a cavitation bubble [2]. The presence of nanoparticles inside the cavitation bubble has been reported [3]. The cavitation bubble kinematics includes expansion, compression, and implosion cycles [4]. It has been reported that nanoparticles are released into the liquid mainly during implosions [5]. The characteristics of nanoparticles such as average size, size distribution, concentration, and stability depend on the parameters of the synthesis. Several studies have been carried out to understand the effect of wavelength [6], repetition rate [7], energy [8], and liquids [9] on the characteristics of colloids with metallic nanoparticles. However, there are few studies on the effect of a magnetic field applied during synthesis on colloid characteristics.

A transverse magnetic field to the propagation direction of a plasma affects the charges (ions and electrons) and leads to the generation of currents [10]. The currents can confine and energize the plasma due to the appearance of forces opposed to the plasma propagation direction and a Joule effect, respectively [1, 10]. Ping et al. [11] reported that applying a transverse magnetic field (1.1 T) during the expansion of a plasma of an AlLi alloy in vacuum leads to an increase in plasma lifetime. Kim et al. [12] reported that applying a magnetic field (0.39 T) perpendicular to the direction of propagation of a silver plasma expanding in deionized water increases the lifetime of the plasma. It has been reported that applying a transverse magnetic field (up to 0.3 T) during ablation of a copper target at atmospheric pressure causes an increase in the amount of material extracted due to magnetic confinement [13].

The optimization in the synthesis of metallic colloidal nanoparticles obtained by laser ablation is a subject of constant research due to its different applications [14, 15].

In this work colloids with gold nanoparticles were obtained, considering the technique of pulsed laser ablation in bidistilled water and the presence or absence of a transverse magnetic field of 0.3 T (perpendicular to the incident direction of laser pulses) during the synthesis. Colloids with silver nanoparticles were obtained under similar conditions. For gold and silver colloids, the effect of magnetic field on concentration, distribution of hydrodynamic sizes, and zeta potential was studied.

Methodology

Figure 1 shows the experimental system used to demonstrate the effect of magnetic field on colloids obtained by laser ablation in liquids. Pulsed laser radiation from a Nd:YAG laser (Quantel Q-smart 450) was directed and focused on the surface of a submerged metallic target. The laser parameters were 1064 nm wavelength, 10 Hz repetition rate, 10 ns pulse duration, and 37 mJ pulse energy. To direct and focus the laser radiation, a laser reflective mirror and a convergent lens of 10 cm focal length were used, respectively. A gold plate of 1.5 cm x 1.5 cm x 0.1 cm

(99.9 % purity) and a silver plate of 1 cm x 1 cm x 0.3 cm (99.99 % of Sigma Aldrich) were used as targets. Each target was placed inside a beaker and submerged in 10 mL of bidistilled water. The beaker was mounted on a rotating system (6.5 revolutions per minute), to avoid laser ablation of the target in a single area and to gently shake the liquid during synthesis. The synthesis time was 10 minutes. To study the effect of a transverse magnetic field (perpendicular) to the incidence direction of the laser pulse and parallel to the surface of the target, the system was located in the center of a pair of coils (electromagnet). The magnetic field was uniform at the position of the target and had a value of 0.3 T. This allowed to compare colloids with gold and silver nanoparticles obtained in the absence of magnetic field with colloids obtained in the presence of the transverse magnetic field.

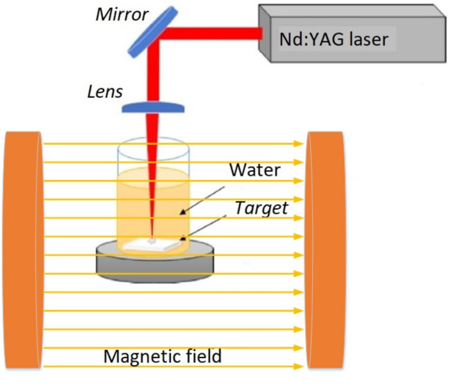

FIGURE 1. *Experimental system used for the synthesis of metallic colloids. The magnetic field (0.3 T) was transverse to the incident direction of laser pulses and parallel to the surface of the submerged target. To obtain the colloids in the absence of a magnetic field, the electromagnet was disconnected.*

To find the colloid concentration, the inductively coupled plasma optical emission spectroscopy technique was considered, a Prodigy XP Vista Dual - Teledyne Leeman Labs device was used. To obtain absorption spectra, an Analytik-Jena Specord Plus 250 equipment was used. The distribution of hydrodynamic sizes and zeta potential were obtained using a Nicomp Nano Z 3000 equipment.

Results and discussion

Figure 2a and Figure 2b show the absorption spectra of the colloids with gold and silver nanoparticles, respectively. In each spectrum, a single peak related to localized surface plasmon resonance (in the visible region of the electromagnetic spectrum) is evidenced. Similar absorption spectra have been reported for approximately spherical metallic nanoparticles obtained by laser ablation in liquids [16–18]. The absorbance values in the wavelengths range for interband transitions are directly proportional to the concentration [7, 19]. Therefore, these figures suggest that applying a transverse magnetic field (B) of 0.3 T during the synthesis of gold and/or silver nanoparticles leads to an increase in colloid concentration.

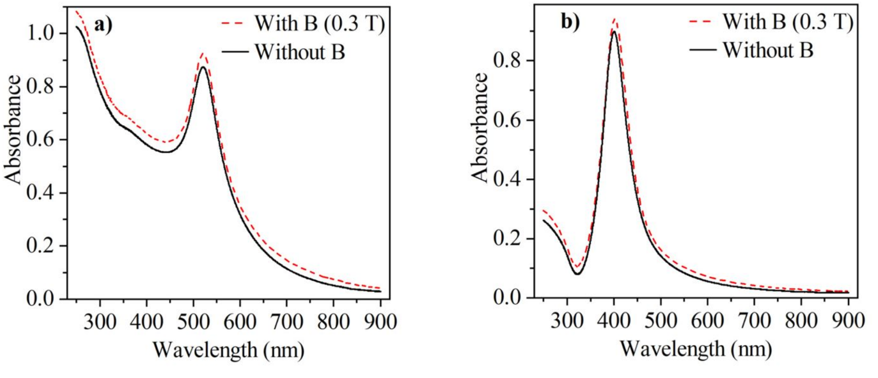

FIGURE 2. *Effect of a transverse magnetic field (0.3 T), applied during the synthesis of colloids with gold (a) and silver (b) nanoparticles, on the absorption spectra.*

Table 1 shows the concentration values for all colloids. Applying a magnetic field of 0.3 T during the synthesis of colloids with spherical gold nanoparticles led to an increase in the amount of extracted material by 11 %. In addition, the effect of the magnetic field on the synthesis of colloids with silver nanoparticles was to increase the concentration by 5 %.

	Au (without B)	Au (with B)	Ag (without B)	Ag (with B)
Concentration (μg/mL)	47.25 ± 0.95	52.25 ± 1.05	22.88 ± 0.46	24.05 ± 0.48

TABLE 1. *Effect of a transverse magnetic field (B = 0.3 T), applied during colloid synthesis, on concentration values. The error of each measure was 2 %.*

Applying a 0.3 T magnetic field during the ablation of a metallic target (gold or silver) immersed in bidistilled water causes plasma confinement. Magnetic confinement gives rise to a plasma of smaller dimensions [1] and with a longer lifetime [11, 12] compared to a plasma generated in the absence of a magnetic field. Magnetic confinement causes an increase in the energy transfer from plasma to target [1, 13]. A plasma (generated by the laser ablation of a submerged solid) located near the target, at a temperature higher than the melting temperature and evaporation temperature of the target, causes material extraction [20–22]. A longer plasma lifetime leads to an increase in the duration of the energy transfer processes from the plasma to the liquid and the target. It is possible that an increase in plasma lifetime may lead to an increase in the amount of extracted material. The cooling of the plasma, due to the transfer of energy from the plasma to the surrounding liquid, causes a cavitation bubble [2]. There are models that relate the dimensions and lifetime of the cavitation bubble with the energy incident on the target [23]. Kim et al. studied the effect of the magnetic field on the dimensions of the cavitation bubble and found no significant changes in the dimensions of the bubble [12]. Therefore, the increase in colloid concentration is due to the magnetic confinement of plasma during synthesis. Magnetic confinement results in a longer plasma lifetime and increases the energy transferred from the plasma to the target.

Table 2 shows the values for Gaussian distributions of hydrodynamic sizes of nanoparticles. The polydispersity (PI), diffusion coefficient, and size distribution based on intensity, volume, and number are shown. The table shows a small decrease in the mean hydrodynamic diameter (D_h) of nanoparticles due to the effect of the magnetic field.

Sample	P.I	Diffusion coefficient (cm^2/s)	Intensity weighted Gaussian distribution		Volume weighted Gaussian distribution		Number weighted Gaussian distribution	
			D_h (nm)	σ (nm)	D_h (nm)	σ (nm)	D_h (nm)	σ (nm)
Au (without B)	0.27 ± 0.01	$5.9 \times 10^{-8} \pm 9.7 \times 10^{-10}$	74.7 ± 1.3	39.1 ± 0.7	33.5 ± 1.4	17.6 ± 0.4	15.8 ± 0.8	8.3 ± 0.3
Au (with B)	0.30 ± 0.01	$5.8 \times 10^{-8} \pm 6.1 \times 10^{-10}$	75.2 ± 0.8	40.9 ± 0.7	31.7 ± 1.1	17.2 ± 0.3	14.7 ± 0.6	8.0 ± 0.2
Ag (without B)	0.29 ± 0.01	$4.9 \times 10^{-8} \pm 6.4 \times 10^{-10}$	90.1 ± 1.2	48.8 ± 0.3	38.8 ± 0.9	21.0 ± 0.4	17.8 ± 0.4	9.7 ± 0.2
Ag (with B)	0.31 ± 0.01	$5.3 \times 10^{-8} \pm 7.1 \times 10^{-11}$	82.4 ± 0.1	45.8 ± 0.6	33.6 ± 0.6	18.7 ± 0.1	15.4 ± 0.3	8.6 ± 0.1

TABLE 2. *Effect of a transverse magnetic field (0.3 T) on the distribution of hydrodynamic sizes of colloids with gold and silver nanoparticles.*

Figure 3a and Figure 3b show the volume-weighted Gaussian distribution for gold and silver nanoparticles, respectively. These figures suggest that size distributions do not show significant differences. The process of colloid synthesis when considering laser ablation in liquids technique is complex. During the synthesis, the nanoparticles present in the laser pulse path absorb and/or scatter the incident radiation, causing the incident energy on the target surface to decrease as the number of pulses increases [24]. In addition, laser radiation absorption may cause agglomerations and/or fragmentations of nanoparticles [25, 26]. It has been reported that during the synthesis, nanoparticles are initially inside the cavitation bubble [3]. During the expansion and compression of the cavitation bubble, nanoparticles experience different temperature and pressure values that can affect the characteristics of the nanoparticles [5]. All these mechanisms, together with the presence of a transverse magnetic field during synthesis, complicate the identification of the possible effect of the magnetic field on the distribution of the sizes of the nanoparticles. Table 3 shows the zeta potentials of colloidal metallic nanoparticles. These potentials are negative and can be considered as stable colloids.

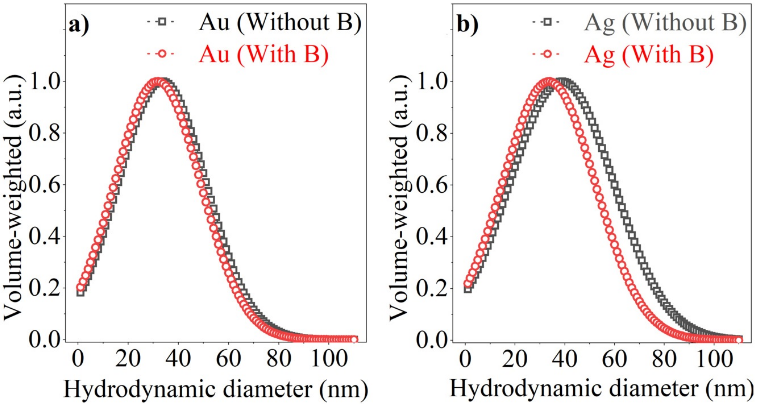

FIGURE 3. *Effect of a transverse magnetic field (0.3 T) on the distribution of hydrodynamic diameters, obtained by considering the volume of the gold (a) and silver (b) nanoparticles.*

	Au (without B)	Au (with B)	Ag (without B)	Ag (with B)
Zeta potential (mV)	(-30.9 ± 2.2)	(-31.2 ± 2.0)	(-27.4 ± 3.1)	(-37.4 ± 3.6)

TABLE 3. *Effect of a transverse magnetic field (0.3 T) on the zeta potential values of colloids with gold and silver nanoparticles.*

Conclusions

Applying a magnetic field during the synthesis of nanoparticles by laser ablation of submerged metallic samples led to an increase in the concentration of the colloids due to the magnetic confinement of plasma. There was no significant effect of the magnetic field on the distribution of hydrodynamic sizes and zeta potential of colloids due to complex processes that occur during the synthesis, which are related to the absorption of radiation by nanoparticles.

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