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High Frequency Electrical Discharge Plasma Used for Synthesis of NanoParticle and Study on Nanoparticle's Size Distribution

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Abstract

- Spark discharge method (SDM) is a useful way for synthesis of nanoparticles. Unlike conventional methods for metal nanoparticles synthesis, SDM method does not require application of chemical surfactants and stabilizers. In recent years, a few articles have investigated physical properties of electrical discharge plasmas used for nanoparticles formation. The aim of this article is the study of spark discharge plasma parameters by means of Optical Emission Spectroscopy (OES) and relation of these parameters with input electrical power and size distribution of gold nanoparticles. We studied spark electrical discharge plasma by stark broadening of hydrogen atoms. The spectrums contain a strong line of H_α and other lines originated from cracking of dielectric media by plasma and the lines originated from gold electrodes contamination. The effects of three dielectric medium are explored i) Deionized water, ii) Absolute ethanol and iii) Air. Furthermore the effect of input pulsed electrical power on plasma density and it's relation to density and size distribution of dispersed gold nanoparticles in liquid was investigated. Surface Plasmon resonance, SEM, XRD, and dynamic light scattering methods were used for investigation of nanoparticles. There were reasonable relation between OES experiment results and both input electrical power and gold nanoparticles distribution.

Key words: Dynamic Light Scattering, FWHM, Optical Emission Spectroscopy, Stark Broadening, Spark Discharge plasma, Surface Plasmon Resonance.

Introduction

In recent years, many articles have been published about the chemical methods of nanoparticle synthesis. But there are a few papers that have investigated the physical methods for nanoparticle synthesis [Burakov (2007), Tien-Der (2008)]. Among physical methods, the electrical discharge method is a reproducible and economical method for nanoparticle synthesis. In addition most arc electrical discharge methods use a high current with low frequency for nanoparticle synthesis [Burakov (2008)].

In this article, we introduced the SDM (Spark Discharge Method) for nanoparticle synthesis that uses the spark transient regime. The advantage of SDM method over arc discharge method is the higher level of controllability. However, a few articles investigate the electrical discharge plasma that is used for nanoparticle synthesis [Descoeudres (2004), Burakov (2009)]. The aim of this paper is the study of SDM by Optical Emission Spectroscopy (OES). The plasma parameters such as electron density in plasma (n_e) were obtained by measuring stark broadening of H_α line in different medias. Also the relation between electron density in plasma, input power and nanoparticle formation were investigated.

Experimental setup:

In this experiment we used a high voltage pulsed power supply for the production of spark discharge plasma in *100 ml* liquid dielectric. The electrodes were gold with high purity (*99/999%*, Aldrich). The gap between electrodes was controlled by means of a DC Motor. Figure 1-a) shows a schematic diagram of electrical circuit.

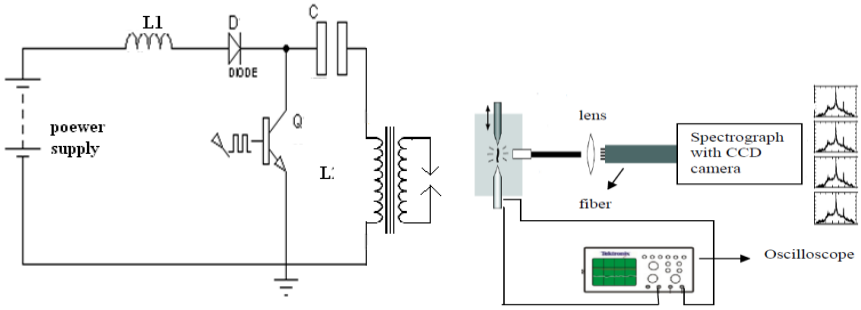


Figure 1, a) *schematic diagram of electrical circuit for nanoparticle synthesis.* b) *Schematic diagram of experimental setup for spectrometry.*

The spark discharge frequency was *14 kHz*. This frequency range was suitable for discharge. The duration of discharge was about *5 ns*. We used a Tektronix 2024 oscilloscope for measuring input power to the plasma. The *V, I* characteristic was measured respectively by means of high voltage probe and Rogowski coil. Also the emitted light from plasma is focused by a lens and was analyzed by an Ocean Optics (HR 2000) spectrometer with a resolution of 0.48 nm. A schematic diagram of experimental set up for the spectrometry is shown in figure 1-b.

Results and Analysis

Study of spark discharge plasma:

Here, the results from spectrums in three dielectric medias were studied. The resulted spectrums are shown in figure 2.

a) Deionized water

b) ethanol

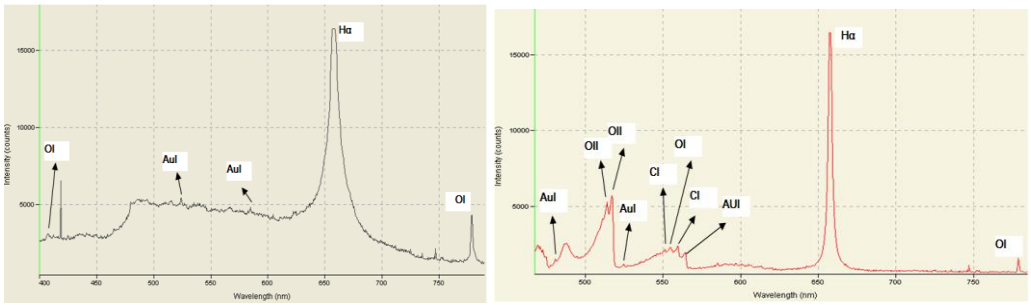


Figure 2.*optical emission spectrum of spark discharge* a) *deionized water* b) *ethanol.*

The presence of various spectral lines is originated from excited species by transition from excited states to the lower states [Griem (1964), Fortov (2000)]. The excitation of these particles is mostly because of collisions of energetic electrons with them. The emitted light from these particles is the spectral characteristic of these particles that identifies them. The presence of some of the lines is because of dielectric molecules cracking by plasma. The strong line of H_α is observed in all spectrums that shows the presence of hydrogen in three dielectric medias. All information about spectral lines was obtained from NIST database. In fact, the stark effect in plasma is because of spectral lines broadening by micro-electric field of plasma. By increasing of the plasma density the exerted inter particle electric field increases, this incidence causes the splitting of subatomic bands [Griem (1964)]. Other broadenings such as: 1) Doppler broadening, 2) Vanderwales broadening and 3) pressure broadening are negligible in our experimental condition [Burakov (2009)]. The lorentzian fit of H_α line and the shift of it's peak shows the important role of stark broadening [Griem (1964)]. By measuring stark broadening of H_α line ($\Delta\lambda$), the plasma electron density (n_e) was calculated. The FWHM of H_α line is proportional to microelectric field strength of plasma (F_0). The relation between $\Delta\lambda$ and F_0 is [Burakov (2009)]:

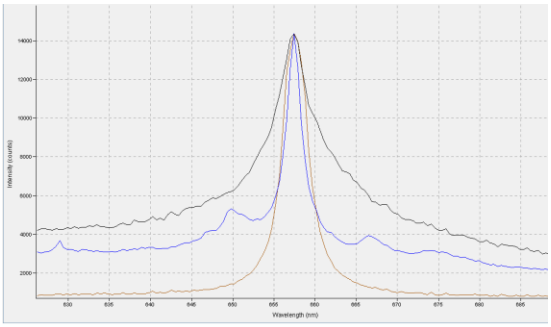
$$\Delta\lambda=2.5\times 10^{-9}\alpha_{H\alpha}n_e^{2/3}. \quad (1)$$

Where $\Delta\lambda$ (nm) is stark broadening of H_α line, n_e is the electron density and $\alpha_{H\alpha}$ is the stark broadening parameter for temperature range of spark discharge plasma. The $\Delta\lambda$ is obtained by Lorentzian fit of H_α line. Stark broadening of H_α line for plasmas in three dielectric medias: 1) deionized water, 2) ethanol and 3) air are obtained from Eq. 1 is given in table 1. As it is obvious from figure 3 the broadening of H_α line in deionized water is more than others and the H_α line broadening for ethanol is more than air. Thus plasma electron density in the water is greater than plasmas in the ethanol and air, and electron density in the ethanol is more than air plasma. This fact is reasonable that electron density in plasmas in liquids is more than air [Burakov (2009)]. The $\Delta\lambda$ and also calculated n_e from Eq. 1 are given in table 1.

dielectric	$\Delta\lambda$(nm)(FWHM)	n_e $*10^{16}(cm^{-3})$
Deionized water	4.96	114.55
ethanol	3.76	73.55
air	2.60	40.36

1.deionized water
2. air
3.Ethanol

1
2
3



H_α line,
in different

Figur3**.** *Comparison of stark broadening for H_α line comes from plasmas in 1) deionized water, 2) ethanol, 3) air.*

Moreover the effect of input pulsed power on stark broadening of H_α and plasma electron density was investigated. Broadening of H_α line with increasing electrical power was shown in figure 4 and the result is given in table 2 and figure 5. As it is obvious, by increasing the input electrical power, these quantities increase until 94.5 kW that the plasma electron density saturated. It is most likely because of the rate of electron production and recombination becomes proportional with the input electrical power and as a result the plasma becomes saturate [Fortov (2000)].

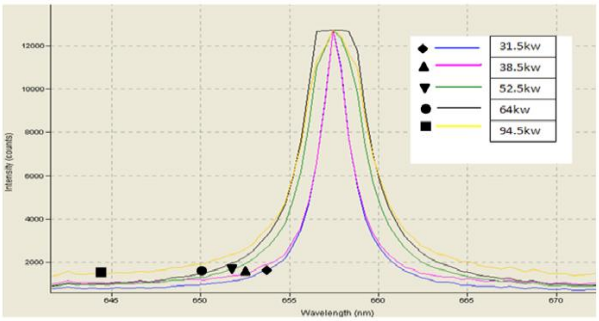


Figure4. *H_α broadened line in a range of pulsed power from 31.5kw -94.5kw*

Power(kW)	24	31.5	38.5	52.5	64	94.5
$\Delta\lambda$(nm)(FWHM)	1.99	2.03	2.61	3.62	4.32	4.20
$N_e*10^{16}(cm^{-3})$	26.71	27.42	41.03	69.25	91.17	87.57

Table2. *Variation of* 1) *stark broadening ($\Delta\lambda$),* 2) *electron density (n_e), with increasing pulsed power in plasma.*

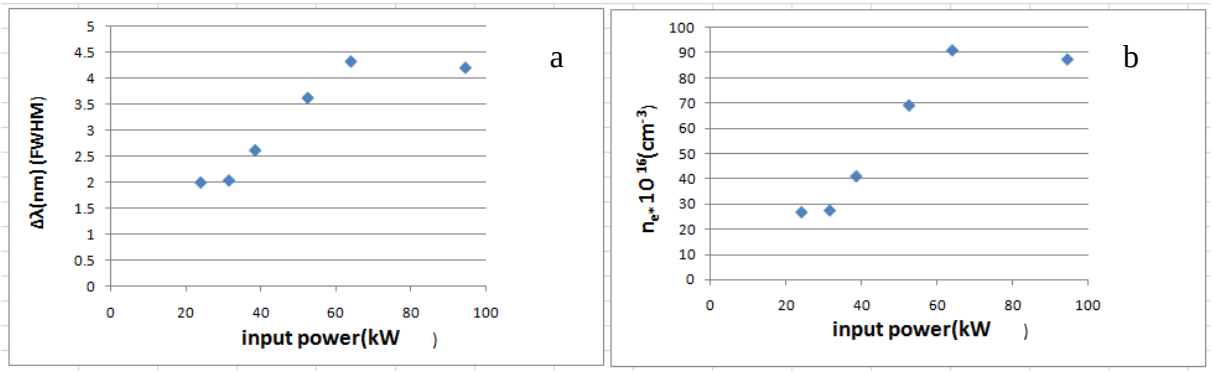


Figure 5. a) *Variation of* $\Delta\lambda$ *(nm) with input pulsed power,* b) *variation of* n_e *(*$10^{16}(cm^{-3})$*) with input pulsed power.*

Synthesis and study of gold nanoparticles:

By applying the high voltage between electrodes led to gold nanoparticles formation. In fact by applying the high voltage, spark discharge plasma between two electrodes makes plasma. The high temperature of plasma causes evaporation of gold electrode. These metal vapors condense and disperse in the liquid [Tien (2008)]. In fact, when the sputtered particles from the electrode reach to a critical radius (r^*), nucleation and growth mechanisms cause formation of nanoparticles [Zhi-qiang (2006)].

As it is shown in the spectrums, the spark discharge plasma in deionized water and ethanol initiates cracking of dielectric molecules. The Colloidal gold nanoparticles that are synthesized by SDM method have good stability without adding any surfactant or capping agent for stabilizing and preventing from agglomeration. We can deduce that ethanol and deionized water molecules decompose into hydrogen, oxygen and their derivatives (R-COH, R-COOH, OH). Hydrogen and oxygen start to interact with gold nanoparticles [Tien (2008)]. The -OH agent in dielectric medias makes the hydrogen bonds with the adsorbed oxygen molecules on the surface of gold nanoparticles. Figure 6 shows the gold nanoparticle micelle that is suspended in ethanol and deionized water.

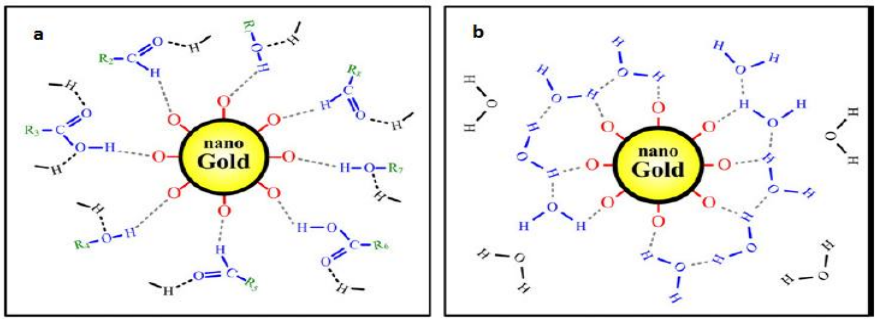


Fig 6.*The Models of gold nanoparticle suspended in* a) *ethanol* b) *deionized water* [Tien (2008)].

Dynamic light scattering (DLS) method is used for measuring size distribution of gold nanoparticles. This method is a useful way to study nanoparticles in colloidal form. Figure 7

shows size distribution of colloidal gold nanoparticles in ethanol in different input electrical power that is obtained by DLS analysis. We studied the nanoparticles size distribution by DLS analysis at *4kW, 10 kW, 14kW 18kW, 24 kW, 31kW, 38kW, 52kW, 64 kW, 94 kW, 110 kW input* power. The result comes in figure 7. Results show that nanoparticles size distribution increases by applying higher input powers.

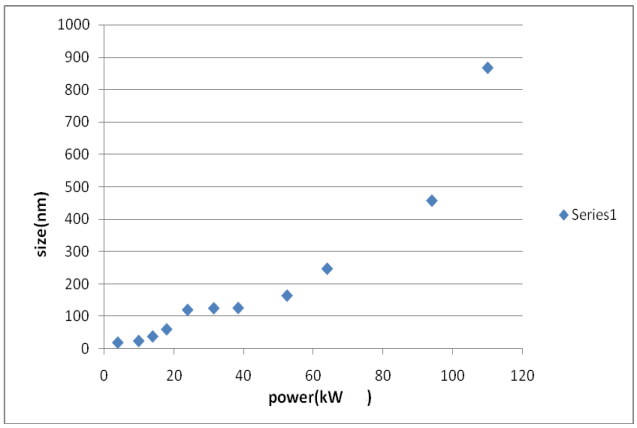


Fig.7. *Size distribution of colloidal gold nanoparticles obtained by DLS analysis in ethanol as a function of different powers.*

In figure 8-a relative absorbance intensity of gold nanoparticles in different input power is presented. As it is obvious from figure 8, by increasing input power the population peak shifts to higher particle size. In higher input electrical power, the anode erosion increases that cause formation of large size nanoparticles, up to 868 nm diameter. In fact in higher electrical powers evaporation rate of gold atoms increases which leads to formation of large size nanoparticles [Kassaee (2010)]. We can deduce that, increase in plasma electron density is the reason of rise of evaporation rate. In fact since these electrons accelerate toward the anode and sputter and evaporate the electrode, thus by rising plasma electron density the rate of evaporation and consequently the rate of nanoparticles formation rises. So with increasing input electrical power and consequently increase of electron density in the plasma (as it is shown in figure 4 and figure 5-b) nanoparticles density in liquid should be increased. We studied this postulation by measuring the comparative density by means of surface Plasmon resonance (SPR) analysis. Since all spectrums were obtained from colloidal gold nanaoparticles in ethanol, the effective parameters in the SPR spectrums are particle size distribution and nanoparticles density [Tien-Der (2008)]. Figure 8-a) shows the SPR spectrum absorbance intensity versus wavelength. As it is shown in figure 8b, the spectrums peaks are around 525 nm that is the characteristic of gold nanoparticles [Sánchez-Ramírez (2002), Ashkarran (2009)]. We studied 3.75 kW, 8.75 kW, 24 kW, 3.15 kW, 38.5 kW, 52.5 kW, 64 kW and 94 kW in the same synthesis time (40 min) for each experiment for SPR analysis.

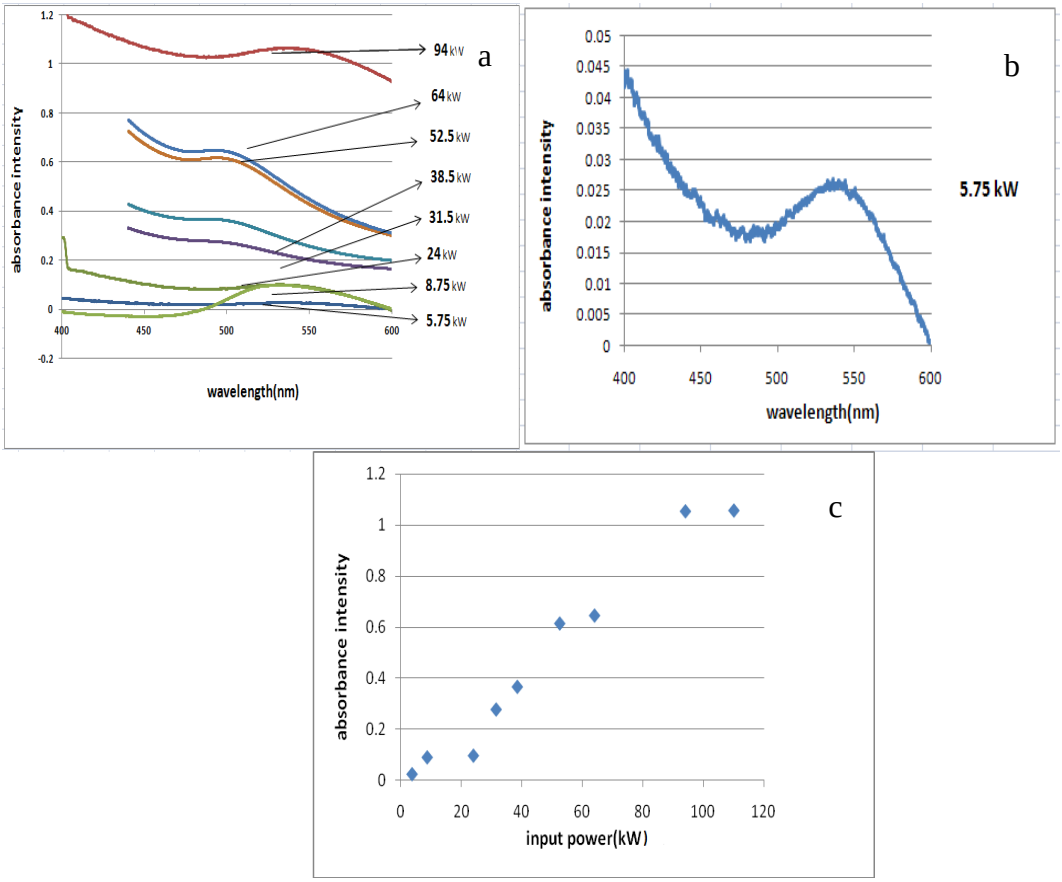


Fig.8-a). *Relative absorbance intensity of gold nanoparticles at 5.75, 8.75, 24, 31.5, 38.5, 52.5, 64 and 94 kW. b). SPR spectrum of gold nanoparticle in ethanol at 5.75 kW input pulsed power. c) Plot of absorbance intensity of SPR spectrum versus input pulsed power.*

As it is shown in figure 8-b by increasing input pulsed power the absorbance intensity increases that is the sign of increase of nanoparticles density in the liquid with increasing pulsed power. Studying on the plot of figure 8-c and electron density plotted in figure 5-b shows a reasonable relation between plasma electron density and gold nanoparticles synthesis rate.

Formation of the gold nanoparticles is confirmed by x-ray diffraction pattern (figure 9).

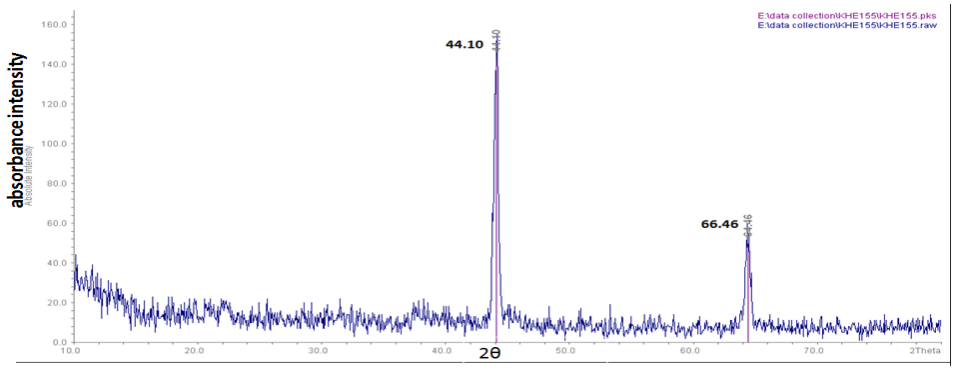


Fig 9. XRD pattern of gold nanoparticles.

The XRD analysis shows the intense peak of (111) and (220) planes of face centered cubic (FCC) lattice of gold nanoparticles. The presence of intense peak of (111) plane indicates that most of gold atoms in the FCC lattice are in the same orientation and approximately are single crystal. Figure 10 shows the SEM images obtained from colloidal gold nanoparticles at 60 kW input power in 1) deionized water 2) ethanol. The gold nanoparticles size obtained from SEM images are in good agreement with DLS analysis.

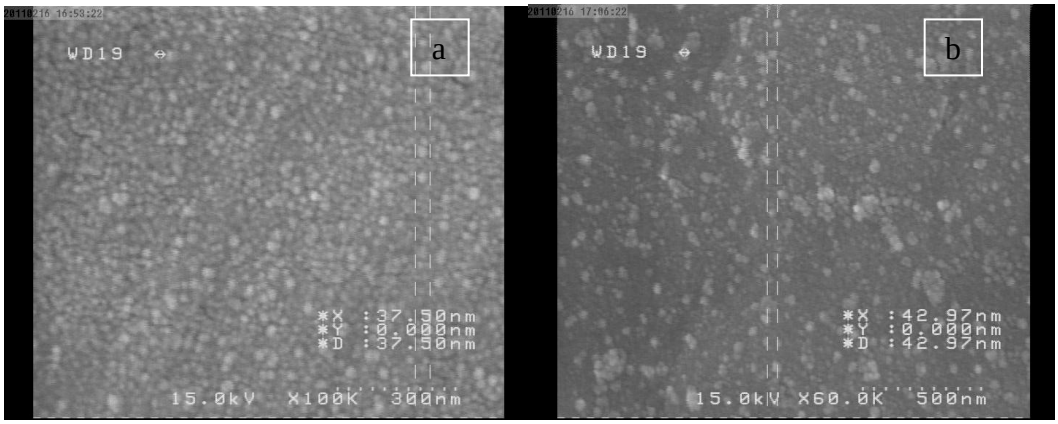


Fig 10. SEM images of gold nanoparticles in a) deionized water b) ethanol.

Figure 10 shows that the gold nanoparticles have spherical shape with average diameters of 37 nm in deionized water and 42 nm in ethanol.

As it is mentioned previously spark discharge plasma in deionized water is denser than plasma electron density in ethanol. SEM images show the consequences of this fact. As it is obvious in figure 10 the nanoparticles density in deionized water is more than the gold nanoparticles density in ethanol. This fact is due to the higher electrode evaporation rate in deionized water. As it is obvious from figure 10 by applying the same physical condition, nanoparticles size in deionized water is smaller than nanoparticles in the ethanol. This fact shows the effect of dielectric media on the aggregation of nanoparticles.

Conclusion:

In this paper we investigated the spark discharge method for preparation of the gold nanoparticles in deionized water and ethanol. Electron density was calculated via stark broadening of H_α line by means of OES method. Moreover, the effect of input pulsed power on size distribution and density of nanoparticles were investigated. The results obtained from OES, DLS and SPR analysis was in reasonable agreement. The presence of gold nanoparticles was confirmed by XRD and SEM analysis.

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