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Synthesis of Au Nanoparticles by Thermal, Sonochemical and Electrochemical Methods: Optimization and Characterization

H. Ashassi-Sorkhabi*, B. Rezaei-moghadam, E. Asghari, R. Bagheri and L. Abdoli
Electrochemistry Research Laboratory, Department of Physical Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran
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The present study concentrates on the synthesis of Au nanoparticles (AuNPs) using aqueous solution of Polyvinylpyrrolidone (PVP) and tetrachloroaurate by different methods as thermal, sonochemical and electrochemical reduction. The PVP has been used as a reducing agent and acts as a stabilizer for Au nano particles that obtained as principal product. In all synthesis procedures, the active radicals resulted from degradation of PVP caused to reduce the Au ions in the solution. A design of experiment (DOE) techniques, the response surface methodology (RSM) and Taguchi method have been used to optimize the selected experimental parameters. As the size of produced nano particles depends on the reaction conditions, we studied the effect of some factors such as the concentration of $HAuCl_4$, the molecular weight of PVP and the time interval for the sonoechemical synthesis of nano particles by the RSM. In electrochemical synthesis, the Taguchi method has been used to optimize the three parameters, interval time of synthesis, applied current density and concentration of $HAuCl_4$. Characterization of AuNPs was carried out by Transition electron microscopy (TEM), UV-Vis spectroscopy, and particle size analyser. The average size of synthesized nanoparticles in optimum condition, estimated by the particle size analyser, were about 130 nm, 26 nm and 91 nm in thermal, sonochemical and electrochemical methods, respectively.

Keywords: Au nanoparticle, PVP, RSM, Taguchi, UV-Vis

INTRODUCTION

The researches on the developing of the nanomaterial have been an important subject in the basic science and considerable attention recently has been paid to synthesize and characterize the different materials in the nano scale. In particular, nano sized particles such as gold nanostructures have been a subject of intensive research because of a broad range of their applications in chemical catalysis, nanomedicines, and nanoelectronics [1-3]. So far, there have been many reports in the literature about the synthesis of metal nanoparticles [4,5]. A large number of nanoparticles with different properties can be fabricated through the various preparation routes such as thermal [6], chemical [7,8], sonochemical [9], electrochemical [4,10], and sonoelectrochemical [11] techniques.

A literature review shows that the well-dispersed gold and silver nanoparticles in the aqueous phase *via* the direct electro-reduction of bulk gold or silver ions could be synthesized [12]. Huang *et al*. [2] synthesized electrochemically the gold nanocrystals under the protection of PVP. The PVP acts as both reducing and capping agent. The oxidation of PVP in aqueous solutions is a process that easily occurs at mild conditions. Also, uniform gold nanocubes [13] and gold nanorods [4] were synthesized using electrochemical methods.

Sonochemical synthesis of gold nanoparticles on chitosan was performed in 2007 [9]. Recently, the gold nanoparticles were synthesized *via* radiolytic reduction of Au(III) salts induced by e^- beam or γ- irradiation, using chitosan as a stabilizer [14].

In recent attempt, the design of experiment has been considered to optimize the synthesis parameters. Traditional method such as full factorial design requires considerable amount of work and time to optimize the synthesis factors [15]. Therefore, new trend of statistical approach based on

*Corresponding author. E-mail: habib.ashassi@gmail.com

Taguchi design [16] and response surface methodology (RSM) [17] are used to evaluate the optimum conditions.

The primary aim of this work is to synthesis the AuNPs by three different ways as thermal reduction, sonochemical and electrochemical methods. Secondly, the optimization of sonochemical and electrochemical processes were performed using response surface methodology (RSM) and Taguchi design, respectively. The UV-Vis spectroscopy, particle size analysis and transmission electron microscopy (TEM), were performed to elucidate the characteristic structures of gold nanoparticles.

EXPERIMENTAL SECTION

Reagents and Instruments

All chemicals, including tetrachloroaurate ($HAuCl_4$) and PVP were purchased from Merck (Germany) and were used without further purification. Double-distilled water was used in all experiments for preparation of solutions and other purposes. Dr. Hielscher S400UP ultrasound generator with a titanium horn H22 was used as ultrasound wave source for sonochemical synthesis. A schematic diagram of the three-synthesis setup of AuNPs is shown in Fig. 1.

Electrochemical synthesis was carried out under galvanostatic condition at room temperature using an Autolab PGSTAT 30 Potentiostat-Galvanostat. UV-Vis spectroscopy measurements (200 nm-700 nm) were performed using a HACH DR 5000 at room temperature.

The particle size analyzer (Malvern ZetaSizer NanoSeries) was used to determine the size of AuNPs obtained from three methods. The TEM images were examined using a Leo 906 Transmission Electron Microscope operated at 200 keV.

Thermal Reduction Method

In thermal reduction method, AuNPs were synthesized without using any other reducing agents. In a typical synthesis, 0.25 g PVP (Mw = 1300000) was added to 10 ml of deionized water. Then, 0.3 ml [$HAuCl_4$] = 0.01 M was added and vigorously stirred. The mixture was heated in 30, 50 and 70 °C and was maintained in these temperatures for 30 min, 1 h and 2 h. The color of solutions turned to red after 5 min in all cases indicating the formation of Au nanoparticles.

Sonochemical Method

A solution of (0, 0.2, 0.4, 0.6 and 0.8) g PVP in 10 ml of deionized water was prepared. After complete dissolution of PVP, (0, 170, 340, 510 and 680 ppm) $HAuCl_4$ was dissolved in the solution and was irradiated for 10 min using an ultrasonic field of 24 kHz frequency. The influencing key parameters on the nanoparticles synthesis were the wight of PVP, different concentrations of $HAuCl_4$ and time period of ultrasound irradiation. In order to study the parallel effects of these parameters, central composite design (CCD) coupled with RSM was used to obtain the optimum conditions for AuNPs synthesis. The interaction of the independent variables with each other was investigated by constructing the response surface and contour plots. As the wavelength of maximum absorbance, λ_{max} in UV-Vis spectra of AuNPs intended to be minimize, the smaller sized nanoparticles were produced. The design of experiments

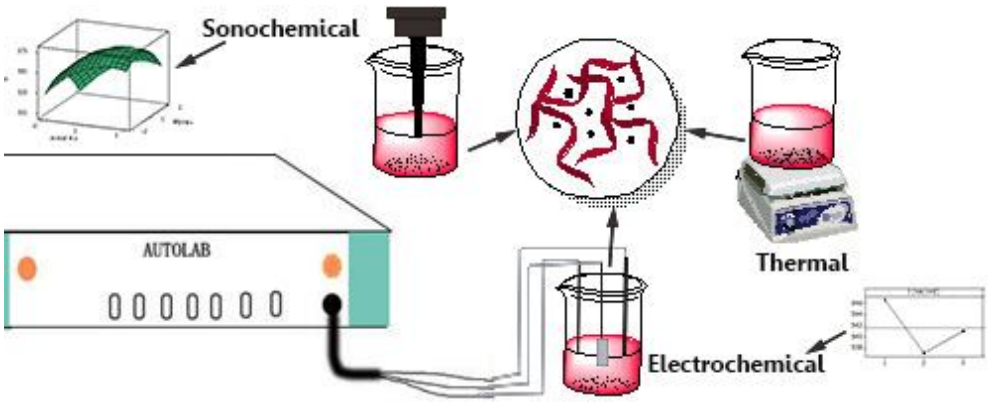


Fig. 1. A schematic diagram of the three synthesis setup of AuNPs.

and experimental data analysis were performed using Minitab 16 software.

Electrochemical Method

A Pt sheet and a platinum rod as counter and working electrodes together with a Saturated Calomel reference electrode (SCE) were used as a three-electrode cell set up to perform the Au nanoparticles. The optimum weight of PVP that used as a stabilizer was determined using the experimental design on the basis of RSM. It was dispersed before all experiments by ultrasonic probe sonication. Experimental design for electrochemical synthesis of AuNPs was carried out based on Taguchi method. The current density, time of synthesis, and concentration of $HAuCl_4$ as Taguchi factors were studied for investigation of the nanoparticle prepration.

Characterization

The Wing-1 (Standard Data Processing) program was used to determine the particle size of AuNPs. In the particle size distribution data graph, the x-axis represents the logarithmic scale of particle diameter (μm) while the y-axis represents the scale of the relative particle amount (%). Samples for TEM were prepared by placing a drop of colloidal sample on coated copper grid and dried at room temperature. As prepared samples were examined using a Leo 906 Transmission Electron Microscope.

RESULTS AND DISCUSSION

Thermal Reduction Method

The UV-Vis spectra of colloidal solution containing AuNPs prepared by the thermal method at different temperatures are shown in Fig. 2. It is revealed that the absorption peak is increased with increasing the temperature. It is obvious that at high temperature the PVP has been degraded and generated free radicals that act as the reducing agents of the gold ions. In addition, at higher temperature degradation of PVP was easier and further. The fact that high temperature would produce more reactive radicals yields more metallic gold particles. Therefore, the yield of thermal reduction has been enhanced by raising the reaction temperature.

The average size of the synthesized nanoparticles estimated by the particle size analyser was about 130 nm.

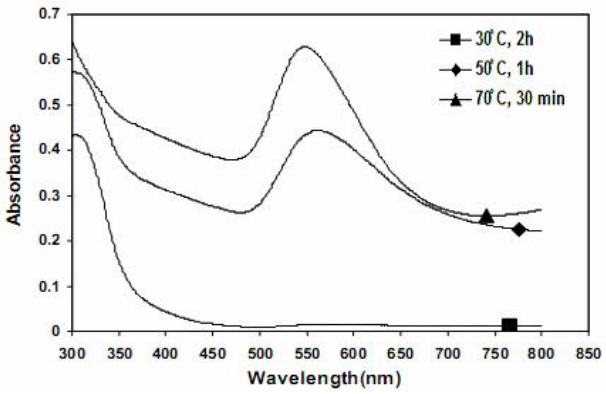
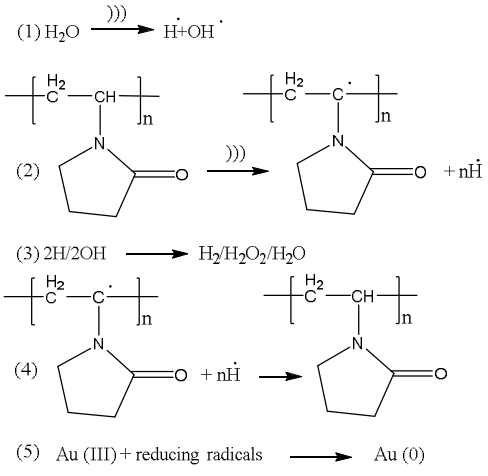


Fig. 2. UV-Vis spectra of colloidal solution containing AuNPs prepared by thermal method at different temperature.

The particle size histograms of Au particles (Fig. 3) show that the particle size distribution of nano particles ranged from approximately 128 to around 167 nm.

Sonochemical Reduction Method

Synthesis. During the sonochemical synthesis of gold nanoparticles, the irradiation of ultrasound may cause to produce more active radicals, by PVP, in the solution to yield more nanoparticles. This was evident from the rapid change of the solution color to red. Different mechanisms were proposed for the synthesis of Au nanoparticles. The radical species, produced by sonolysis of water and PVP, reduce the Au(III) ions and result in the formation of Au nanoparticles. The following ultrasonic irradiation mechanism may be proposed [18,19]:



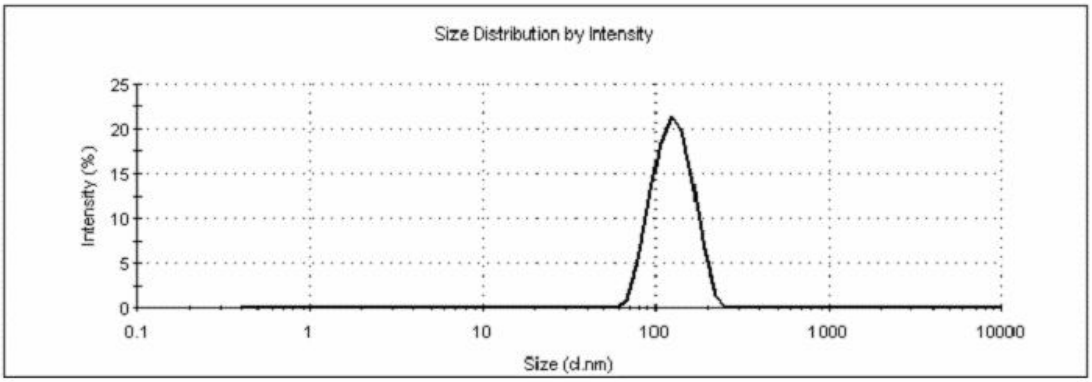


Fig. 3. The particle size histograms of Au particles synthesized by thermal method.

Table 1. Actual and Coded Values of Independent Variables Used for Experimental Design

Factor	Symbol	Level				
		-α[a]	-1	0	+1	+α
Concentration of $HAuCl_4$ (mmol Au^{3+})	X_1	0	0.005	0.010	0.015	0.02
Weight of PVP (g)	X_2	0	0.200	0.400	0.60	0.80
Time (min)	X_3	5	8.00	11.0	14.0	17.00

[a]α = 1.68 (axial point for orthogonal CCD).

Table 2. Applied Central Composite Design Matrix and Predicted Values of the CCD

Run order	Coded values			λ_{max}
	X_1	X_2	X_3	
1	0	0	0	576
2	0	0	0	570
3	0	-α	0	563
4	+1	-1	+1	578
5	+1	-1	-1	583
6	+1	+1	-1	574
7	+1	+1	+1	564
8	-1	-1	-1	536
9	0	+α	0	540
10	-1	-1	+1	549
11	0	0	+α	567
12	-α	0	0	552
13	0	0	0	563
14	0	0	0	572
15	-1	+1	+1	533
16	0	0	0	588
17	0	0	0	556
18	0	0	-α	568
19	+α	0	0	560
20	-1	+1	-1	528

where the symbol,))), corresponds to ultrasonic irradiation. It is well known that the PVP also acts as a stabilizer for the produced AuNPs and suppresses the further growth of the Au nanoparticles. Furthermore, the response surface methodology (RSM) was used to optimize the synthesis parameters influencing the particle size. The studied parameters were the amount of PVP, the sonication time and the initial $HAuCl_4$ concentration.

Response surface methodology (RSM). Central composite design (CCD), which is the most popular response surface method for the experimental design, was applied to optimize the sonochemical synthesis of AuNPs. In this study, three factors have been introduced as RSM input variables which their experimental ranges in coded and actual values are presented in Table 1. Based on CCD design with three factors a set of 20 experiments was carried out by Minitab 16 software (Table 2).

It is well known that as the wavelength of UV-Vis spectrafor maximum absorption of nanoparticles intended to be minimized, the smaller particles are obtained [7,20], therefore, the RSM model was arranged to achieve the smallest λ_{max}. For further explanation, a prominent spectroscopic feature of noble metal nanoparticles (NPs) is the so-called surface plasmon resonance, which gives rise to a sharp and intense absorption band in the visible range. The physical origin of the absorption is a collective resonant oscillation of the free electrons of the conduction band of the metal. For a spherical nanoparticle that is much smaller than the wavelength of the incident light, its response to the oscillating electric field can be described by the so-called dipole approximation of Mie theory [21]. It has been previously established that the surface plasmon of small spherical particles shifts to higher energies (blue shift) as the mean diameter of the particles decreases [22]. According to literature [7,16,22-24], as the surface plasmon band of nanoparticles shifted to the low wavelength (λ_{max} in UV-Vis spectra), the smaller sized nanoparticles were produced. Therefore, in this work the authors showed that a

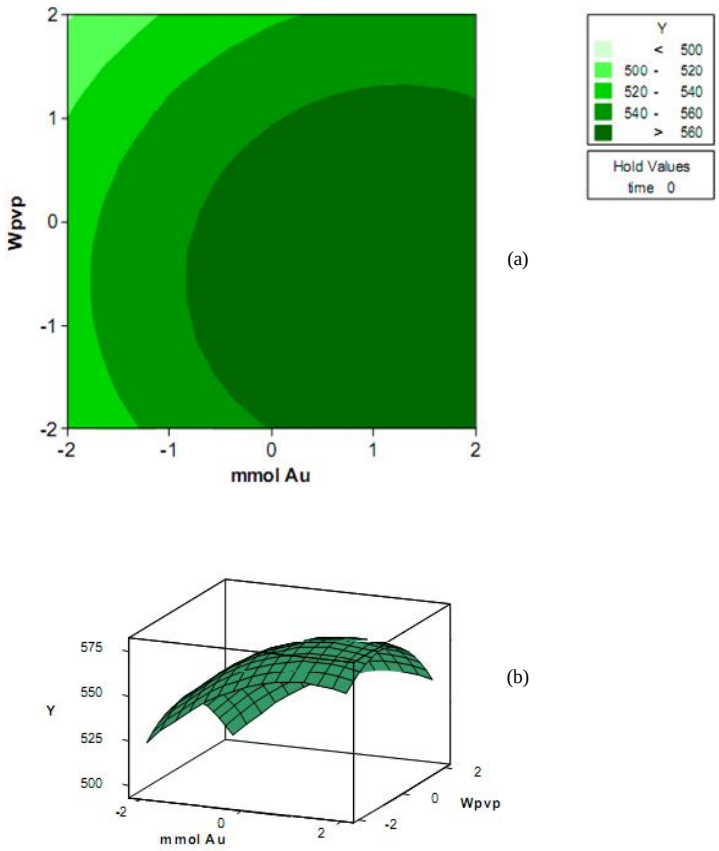


Fig. 4. (a) Contour and (b) Surface plots of weight of PVP *vs.* Au ions concentration.

change in the synthesis condition leads to a shift in the measured maximum of the surface plasmon resonance band. Since our object is to find the smaller AuNPs in optimization processing we focused on the discovering of minimum amount of λ_{max} in UV-Vis spectra.

On the other hand, the interaction of the independent variables was investigated by constructing the response surface and contour plots based on the effects of the levels of the corresponding factors. The three-dimensional response surfaces and two dimensional contour plots over independent variables are shown in Figs. 4-6. It is obvious that the Plasmon absorption band decreases by increasing the amount of PVP and decreasing the concentration of $HAuCl_4$. This behavior can be seen in three-dimensional surface plot (Fig. 4b). It can be said that in the presence of higher amount of PVP, the produced radicals increased and the reduction rate of Au(III) ions to metallic gold has been grown. On the other hand, as suggested in the literature, the higher reduction rate can cause to obtain the smaller nanoparticles [25].

Figure 5 presents the response surface and contour plots for Plasmon absorption band as functions of the irradiation time and concentration of the $HAuCl_4$. As can be deduced from Fig. 5, a little/a shoet time is needed for synthesis of nanoparticles in lower concentrations of Au. On the other hand, as shown in Fig. 6, the minimum absorption band can be appeared in higher amount of PVP and longer time.

Characterization. The UV-Vis spectra, TEM, and particle size analyser (Zeta Sizer) were used to characterize the synthesized gold nanoparticles. UV-visspectra of AuNPs obtained sonochemically is shown in Fig. 7. A broad Plasmon absorption band, centred on 540 nm in the spectrum, characterised the formation of average size of the colloidal particles.

Figure 8 shows TEM photographs of AuNPs synthesized

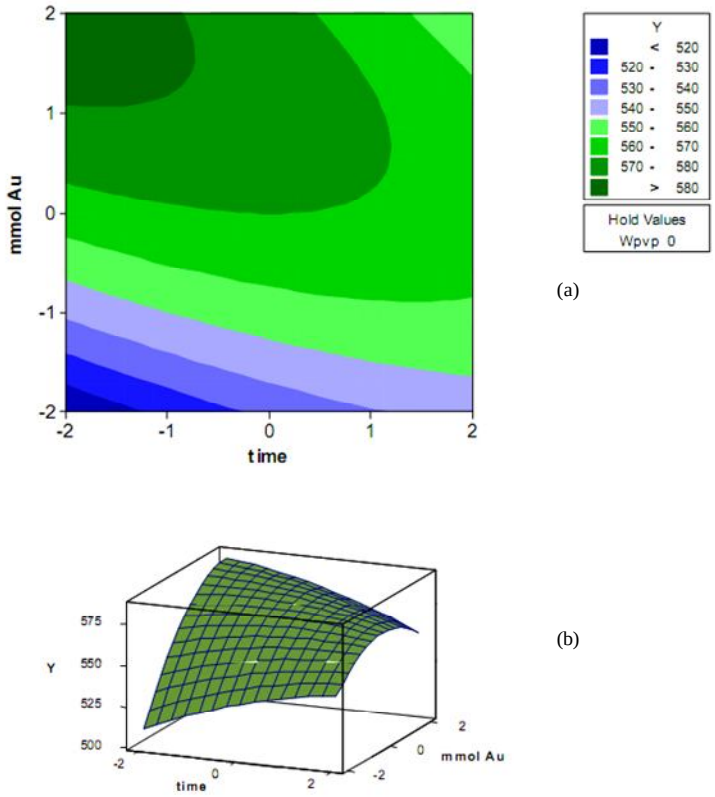


Fig. 5. (a) Contour and (b) Surface plots of Au ions concentration vs. synthesis time.

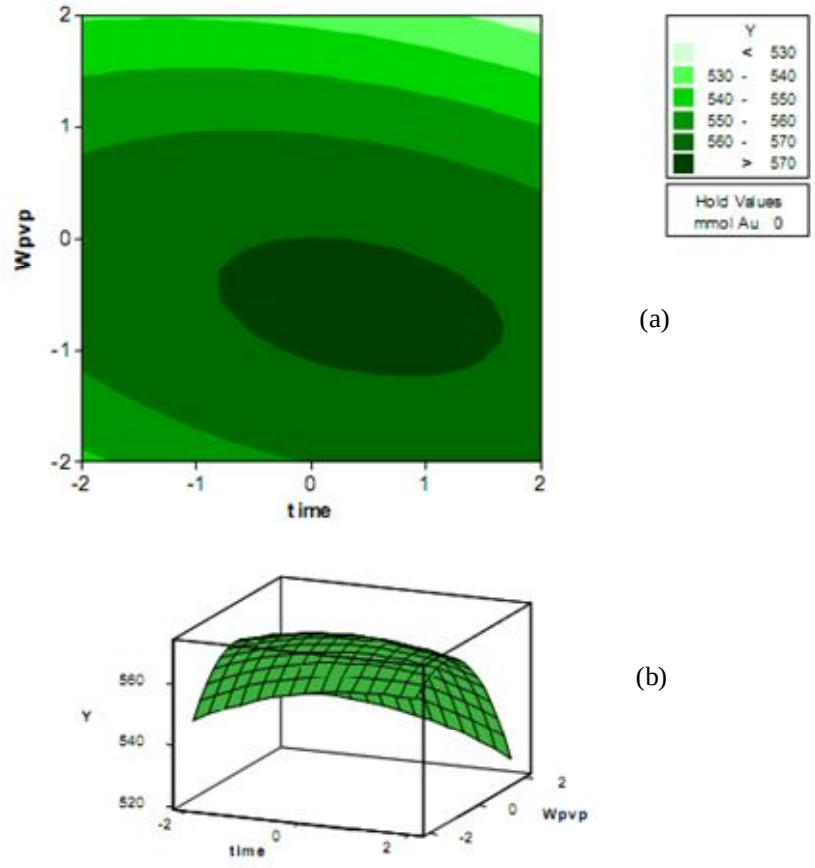


Fig. 6. (a) Contour and (b) Surface plots of weight of PVP vs. synthesis time.

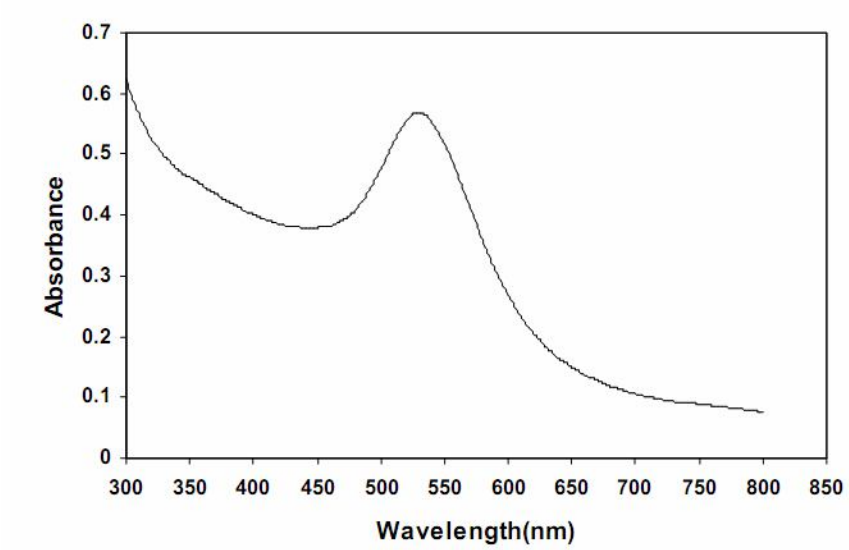


Fig. 7. UV-Vis spectra of AuNPs prepared at optimum condition by sonochemical method.

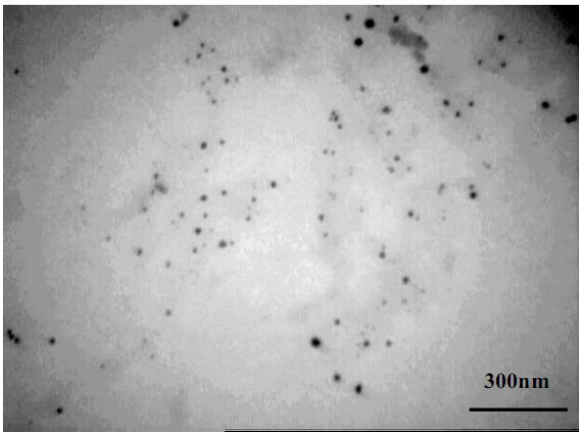


Fig. 8. Transmission electron micrographs of Au particles prepared by sonochemistry after 10 min irradiation.

by the sonochemical method. It was proved that the spherical particles were prepared.

In order to more investigation, the size of nanoparticles has been estimated by the particle size analyzer. The Wing-1 (Standard Data Processing) program was used to determine the particle size of AuNPs at optimum condition (run order: 20, Table 2) and plotted in Fig. 9. The results show that the average size of the synthesized particles is about 26 nm.

Electrochemical Method

Synthesis. In this section, electrochemical synthesis was carried out under galvanostatic condition at room temperature. The aqueous electrolyte solution contains the different concentration of $HAuCl_4$ and optimum amount of

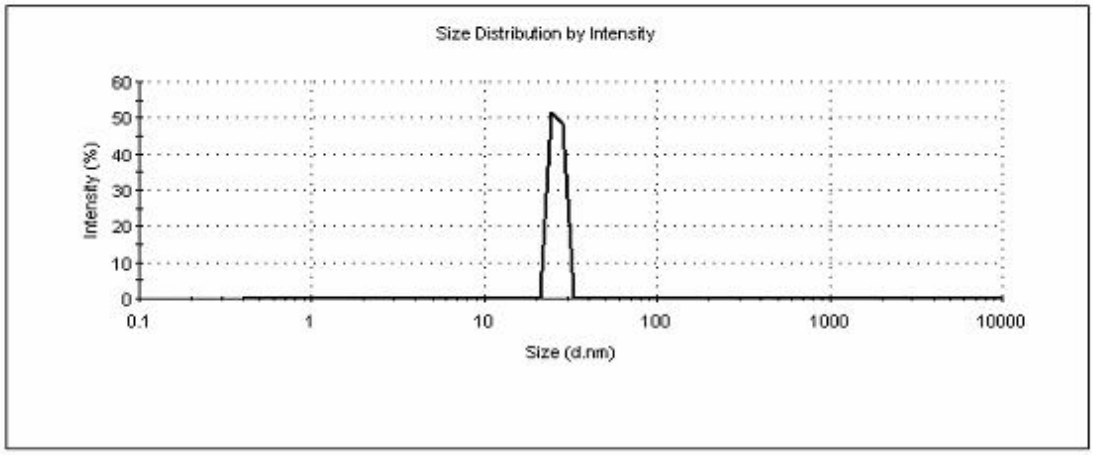


Fig. 9. The particle size histograms of Au particles synthesized by sonochemical method.

Table 3. Design Factors and Levels for Taguchi Design

	Orthogonal Arrays	I (A cm^{-2})	Time (s)	Concentration (ppm)	λ_{max}
1	111	1	600	13.6	549
2	122	1	1200	40.8	550
3	133	1	1800	68.0	541
4	212	2	600	40.8	538
5	223	2	1200	68.0	532
6	231	2	1800	13.6	541
7	313	3	600	68.0	541
8	321	3	1200	13.6	550
9	332	3	1800	40.8	532

PVP as stabilizer. Before all experiments for completely dispersion of PVP, the solutions were sonicated by ultrasonic probe. Taguchi method was used to optimise the different parameters such as current density, time and concentration of $HAuCl_4$ to obtain the favourite condition for the preparation of nanoparticles.

Taguchi design. For electrochemical synthesis of gold nanoparticles, one of the designs of experiment (DOE) technique, the Taguchi method, were used to optimize the three electrochemical parameters (synthesis time, applied current density and concentration of $HAuCl_4$). These parameters were analyzed using three selected levels, shown in Table 3. In the experiments, the factors and levels were used to design an L9 orthogonal array. The Minitab (16) software was used and the average of response at each level for various factors were plotted (Fig. 10). The average λ_{max} values at different levels are summarized in Table 4. Rank values based on Delta statistics, which compare the relative magnitude of effects of the different parameters, show that the applied current density is the most effective one.

As mentioned above, to obtain the smaller particles, the wavelength of UV-Vis spectra of AuNPs has to be minimized. The main objective of the optimization was to evaluate the optimum conditions for synthesis. The optimum condition for AuNPs synthesis, using Taguchi design, was estimated as I = 2 mA cm^{-2}, time = 1800 s and 0.5 M of $HAuCl_4$.

Characterization. UV-Vis spectra of AuNPs prepared at different conditions according to Taguchi design is shown in Fig. 11. It is clear, a broad plasmon absorption band

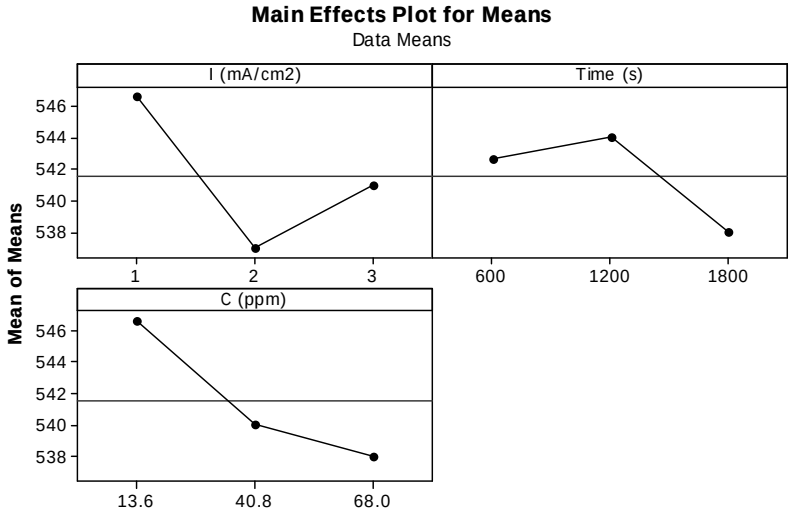


Fig. 10. Effects of (a) current density, (b) synthesis time and (c) $HAuCl_4$ concentration on average λ_{max} values.

Table 4. Response Table for Means

Level	I (mA cm^{-2})	Time (s)	C (ppm)
1	546.7	542.7	546.7
2	537.0	544.0	540.0
3	541.0	538.0	538.0
Delta	9.7	6.0	8.7
Rank	1	3	2

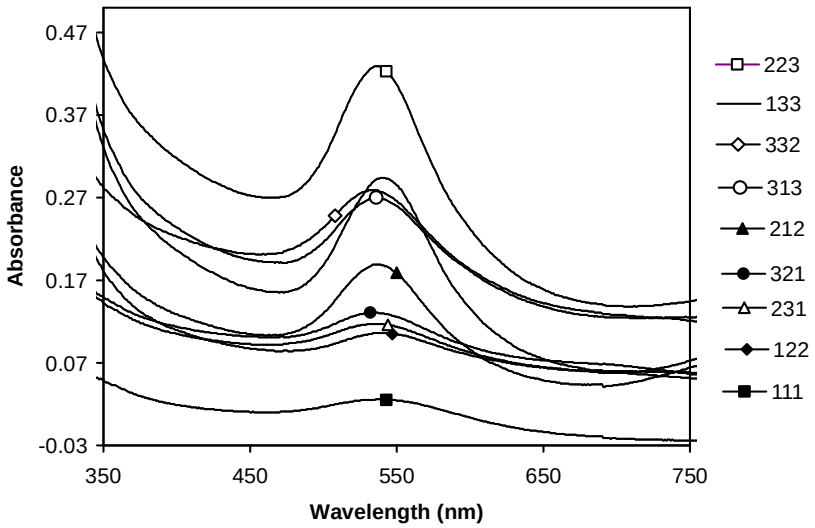


Fig. 11. UV-Vis spectra of AuNPs prepared at different conditions of Taguchi design according to Table 3.

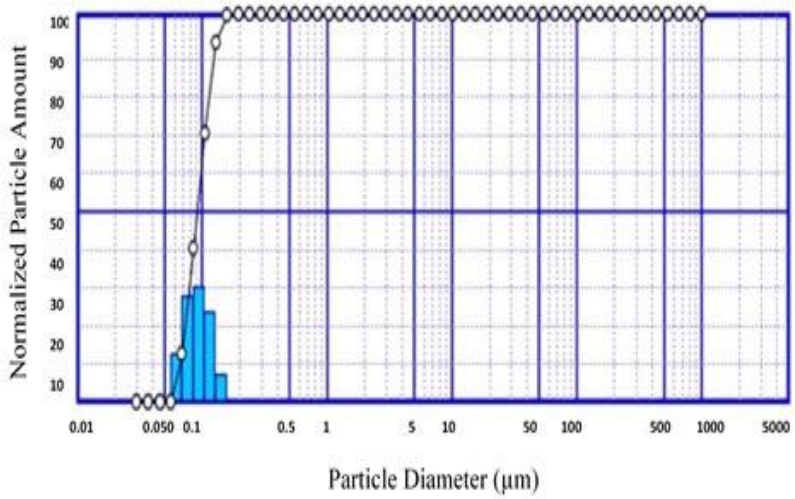


Fig. 12. The particle size histograms of Au particles synthesized by electrochemical method.

centered at 540 nm is observed. A blue shift is also observed as the current density is increased dealing with the particle size decrease. The AuNPs size as-prepared electrochemically, under the optimum condition, was investigated by particle size analyzer and the average size of the synthesized particles was 91 nm (Fig. 12).

CONCLUSIONS

The AuNPs were successfully synthesized by thermal, sonochemical and electrochemical methods. We synthesized AuNPs from simple thermal route in the absence of any reducing agents, and the PVP that has been used as a stabilizer acted as a reducing agent. The studies demonstrated that the reducing rate of Au ion to nano-Au was remarkably enhanced with increasing of the temperature. Also, the size of particles decreased with increasing temperature.

During the sonochemical synthesis of AuNPs from aqueous solution, the conditions were optimized by the

response surface methodology. The effects of the three important operational parameters, the weight of PVP, the sonication interval time and concentration of $HAuCl_4$ were evaluated by the response surface and counter plots. The optimum conditions, proposed by the RSM, for minimizing the particle size were found at high amount of PVP and low concentration of $HAuCl_4$. The average size of the synthesized nanoparticles using this method is estimated to be 39 nm.

The galvanostatic method was successfully employed for electrochemical preparation of AuNPs in the presence of PVP. It is found that the applied current density has an important role on the size of synthesized particles. Taguchi orthogonal array was employed to optimize the current density and other parameters to reach the minimum average size of nanoparticles. The average size of the synthesized AuNPs by electrochemical method was estimated to be about 90 nm.

Consequently the results showed that the particle size of AuNPs obtained by the sonochemical method is smaller than that in both thermal and electrochemical methods. Furthermore, in thermal method a longer time is required to accomplish the reaction.

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