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Structural, Morphological and Optical Properties of Metal Nanoparticles Assemblies of Gold

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Key words: Field Emission Scanning Electron Microscope (FESEM), Gold nanoparticles, Sodium borohydride, surface plasmon resonance, UV-visible spectrophotometer, Transmission Electron Microscope (TEM), 1,9-Nonanedithiol (NDT)

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Abstract: In this research work, gold nanoparticles were synthesized by three different methods. These were, seed growth method, citrate-reduction method and gold nanoparticles prepared from sodium borohydride and refluxed with sodium acrylate. These nanoparticles were characterized using UV-visible spectrophotometer, TEM and FESEM. In the seed growth method gold nanoparticles were synthesized by four steps of seeding growth with maximum plasmon bands at 524, 524, 530 and 539 nm as examined by UV-visible spectrophotometer. The TEM micrograph showed that gold nanoparticles obtained from first step of seeding were spherical with 5-10 nm diameters. The second step nanoparticles were spherical and triangular with diameter of about 15-20 nm. Those obtained from third and fourth step of seeding were spherical with17-20 nm and 50-60 nm size, respectively. As the size of gold nanoparticles was increased from 5-60 nm, their SPR band was also increased from 524-539 nm. The citrate-stabilizedna noparticles were 15-17 nm in size with maximum plasmon band at 521 nm. The UV-visible spectra for the gold nanoparticles synthesized by sodium borohydride in 1,9-NDT showed the appearance of a second red-shifted plasmon resonance band at 950 nm wavelength. The intensity of this band was enhanced with increase in 1,9-NDT concentration.

INTRODUCTION

The word nano (10^{-9}) means small in size is a Greek word. The particles having two or more dimensions with size range of 1-100 nm are called as nanoparticles (ASTM International)[1]. Because of high surface area, nanoparticles have distinctive physical and chemical properties in comparison with the bulk materials. These nanoparticles have many applications in electrochemistry, photochemical, biomedicine, computed tomography, nuclear magnetic resonance imaging and ultrasound as well[2, 3]. Nanoparticles have many handy platforms that can be used for imaging and therapeutic purposes. These platforms can be produced from many inorganic and organic materials. However, the inorganic platforms have more importance for instantaneous therapy and diagnosis because of their easy adjustment, high medication loading capacity and stability as well[4].

Metal nanoparticles have been studied for hundreds of years in modern times primarily due to their unique and interesting optical and catalytic properties. Particularly, gold nanoparticles have attracted a wide range of interest due to increasing applications in sensors, biosensors, medicine, electronics, catalysis and many emerging areas of nanotechnology. These applications require the ability to control the size, shape and surface properties of gold nanoparticles and their assemblies.

The gold nanoparticles have many good physical, chemical and optical properties as given by Pissuwan *et al*.[5]. In the field of biotechnology and biomedical, gold nanoparticles are extensively used due to their large surface area and high electron conductivity[6]. The adaptation of the nanometres is lead to enhance the interaction of these nanoparticles with biological cells[7]. Higher permeability and retention are the distinctive property of nanoparticles to collect and interact with the tumour or cancerous cells. It was found that the gold nanoparticles are safest and much less toxic agents for drug delivery[8]. Gold nanoparticles have many applications such as cancer therapeutics, catalysis and optical molecular sensing.

Gold nanoparticles can be synthesized by different methods[9]. These methods can be biological, physical and chemical method. One of these methods to synthesize gold nanoparticles is laser ablation[10]. Colloidal gold, formed by various methods is used in the medical application. The colloidal gold is synthesized by citrate reduction method[11,12]. Synthetic gold nanoparticles of various structure[13] involving gold nanorods[14], silica-gold nanoshells[15] and hollow gold nanoparticles[16] are also reported.

The gold nanoparticles are non-toxic in nature having large surface area and widely used in biomedical fields[17]. In the vivo cell imaging, gold nanorods are extensively used because of resonance absorption Plasmon and scatter of light in infra-red zone[18]. Moreover, the very small size of colloidal gold nanoparticles have made them more useful to introduce in the tissues and cells of biological molecules like proteins and DNA[19]. Due to the electronic properties, gold nanoparticles have been frequently employed in analytical methods and are being used as an electrode sensor of different samples[7].

To synthesize gold nanoparticles by the chemical reduction process of the $HAuCl_4$ was proposed by Ahmed *et al*.[20]. Thermal citrate reduction is also for the synthesis of gold nanoparticles through Raman Spectroscopy (SERS) by using inositol hexakisphosphate (IP6) to reduce $HAuCl_4$[21]. Moreover, the synthesis of gold nanoparticles is also reported by the tri-sodium citrate and hydrogen tetrachlorocuprate (III) tetrahydrate (chloroauric acid)[22].

The major objective of this research work was to study the surface plasmon resonance, structure and morphology of nanoparticle assemblies of gold, synthesized by chemical reduction method. Gold nanoparticles were prepared by three different methods as seeding growth, citrate-reduction and by sodium borohydride. UV-visible spectrophotometer was used to study the optical properties of gold and shifting of their λ_{max} due to the aggregation of the gold nanoparticle assemblies with ethanol and 1, 9-nonanedithiol. These gold nanoparticles were then analyzed by Transmission Electron Microscope and Scanning Electron Microscope to study the morphology (size and shape).

MATERIALS AND METHODS

Gold nanoparticles are of great interest due their wide range of applications. Several methods have been developed for synthesis of gold nanoparticles of different size and shapes. Gold nanoparticles have been intensively studied among a variety of metal nanoparticles due to their unique optical, electrical and catalytic properties. The present research work was conducted in the laboratory of Nano Biotechnology at NIBGE Pakistan.

Materials: Following analytical grade chemicals were used during this research work. Gold chloride ($HAuCl_4.3H_2O$), Ascorbic acid (Aldrich), Sodium borohydride ($NaBH_4$), Tri-sodium citrate (Fisher), Cetyltrimethylamonium Bromide (CTAB), Sodium acrylate (SA, Aldrich, 97%), Ethanol, 1, 9-nonanedithiol (Aldrich, 95%). For all experiments Milli-Q water (18.1 M) was used, purified with an ultrapure water system Milli-Q Plus 185 (Millipore purification pack).

Synthesis of gold nanoparticles by seeding growth method: Gold nanoparticles were prepared using seeding growth method as reported by Jana *et al*.[23] with few modifications. First the gold nanoparticles of about 3.5 nm were made which were then used as seeds for the synthesis of larger size gold nanoparticles.

For gold nanoparticles seed preparation 20 mL $HAuCl_4$ aqueous solution (0.25mM) was constantly stirred for 5 min at room temperature. After this trisodium citrate (0.25 mM) was added to the gold solution and stirred for more 15 min at room temperature. Next 0.6 mL of ice-cold, freshly prepared, $NaBH_4$ (0.1 M) solution was added under continuous stirring. The solution turned radish pink immediately after the addition of $NaBH_4$, showing gold nanoparticle formation. The resultant nanoparticles keep on stirring for 1 h. These nanoparticles were used as seeds. Then UV-visible spectrum of these seeds nanoparticles was recorded using UV-visible spectrophotometer (CE 7500 Dual beam UV-Visible spectrophotometer).

Growth solution was made by dissolving 1.8 g of cetyltrimethylammonium bromide (CTAB, 0.08 M) in

50 mL $HAuCl_4$ aqueous solution (0.25 mM). The mixture was heated until a warm clear orange color seemed. Freshly made ascorbic acid solution (0.27 mL, 0.1 M) was also added to the mixture. A colorless solution formed which we labeled as the growth solution.

Then this 9 mL of growth solution was added to four 50 mL conical flasks labeled as A, B, C and D. In the flask A 1.0 mL of seed solution was added while stirring vigorously for one minute. It was kept on stirring until the solution turned wine red. After 1 min, 1.0 mL from solution A was taken and added to solution B under vigorous stirring until the solution turned deep red. After 1 min, 1 mL from solution B was taken and added to C while stirring vigorously until the solution turned purplish pink. After one minute 1mL from solution C was taken and added to D. It was kept on stirring vigorously until a brown color was attained. Solution A-D signifies the gold nanoparticles of different size as shown by their colors. The gold nanoparticles (A and B) were centrifuged at 6,000 rpm for 10 min at room temperature and re-dispersed in the deionized water. The gold nanoparticles (C and D) were centrifuged at speed of 14,000 rpm for 20 min at room temperature and re-dispersed in deionized water. All these samples of gold nanoparticles were characterized using UV-visible spectrophotometer and TEM.

Synthesis of gold nanoparticles by citrate reduction method: Anaqueous solution of tri-sodium citrate (5 mL, 38.8 mM) was warmed at (50-60°C) and then added rapidly to a boiling aqueous solution of $HAuCl_4$ (50 mL, 1 mM). The color of the reduction mixture altered to ruby red after a time of 5 min.

We continued the reflux for one hour to confirm the completion of reaction. Then the solution of gold nanoparticles was allowed to cool down to room temperature. The gold nanoparticles were centrifuged at 14,000 rpm for 10 min and stored at room temperature for their characterization.

Synthesis of gold nanoparticles by sodium borohydride: For the synthesis of gold nanoparticles by sodium borohydride, 250 mL of 0.4 mM $HAuCl_4.3H_2O$ aqueous solution was stirred at room temperature. After that approximately 6.25 mL of sodium acrylate (40 mM) was added to the gold solution under stirring. This solution was kept on stirring for about 15-20 min. Then freshly made $NaBH_4$ solution (25 mL, 0.7 mg mL^{-1} of $NaBH_4$) was added at once while stirring vigorously. We observed a dark red color, seemedinstantaneously after the addition of sodium borohydride. This showed the formation of gold nanoparticles. We continued Stirring for at least 4 h for the completion of the reaction.

In order to investigate the controlled aggregation of gold nanoparticles synthesized by sodium borohydride reduction, they were further refluxed with sodium acrylate. It was done to increase the stability of the gold nanoparticlesin NDT/ethanol. Then a warm solution of sodium acrylate (95.24 mL, 40 mM) was added to the boiling gold nanoparticles solution. The color of the solution was changed from dark red to yellowish red. We refluxed these nanoparticles for more 30-40 min and then allowed them to cool down to room temperature. These gold nanoparticles were then centrifuged at 45,000 rpm for 30 min using ultra centrifuge machine at room temperature. The gold nanoparticles before reflux and after reflux with sodium acrylate were then investigatedby using UV-visible spectrophotometer, FESEM and TEM.

Combination of gold nanoparticles with Ethanol and 1,9-nonanedithiol: The concentrated pellets of gold nanoparticles synthesized by sodium borohydide reduction and refluxed with sodium acrylatewere then re-dispersed in 0, 10, 20, 30, 50, 60, 80 and 90% ethanol/water (v/v) mixtures. The gold nanoparticles (200 μL) solution from each of the above stated ethanol/water mixtures was placed in each of the 96-well micro titer plate as shown in the study. The ratio of ethanol was enhanced from zero (pure deionized water) to 90% down the rows (i.e., 0, 10, 20, 30, 50, 60, 80 and 90% ethanol in water were used as the dispersion media in rows 1, 2, 3, 4, 5, 6, 7 and 8 respectively). The quantityof 100 μM NDT was enhanced along the column from left to right. It was increased as 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 μL of NDT and ethanol solution. It was added to the each well in columns 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12, respectively. For the control experiment, no NDT was added to the column 1well. By the adding the required volume of the ethanol/water mixture, the volume of reactant mixture in each well was made up to 300 μL. The reaction was supervised by taking the UV-visible spectra of each reaction after 24 h.

Characterization of gold nanoparticles: The gold nanoparticles prepared by three different protocols of seeding growth method, citrate-reduction method and from sodium borohydride were characterized using Transmission Electron Microscope (TEM), FESEM (JEOL JSM 7500) and UV-visible spectrophotometer (CE 7500 Dual beam UV-visible spectrophotometer) at Nano Biotechnology Lab of NIBGE Pakistan.

Spectrophotometer analysis of gold nanoparticles: The surface plasmon resonance is a unique property of nanoparticles. Due to this property nanoparticles absorb radiation in UV-visible region and have specific colors in solution form depending on their shape,size and the media in which they are dispersed. Nanoparticles smaller in size absorb at shorter wavelength whereas larger particles absorb at longer wavelength.

In this study, UV-visible absorption spectra of gold nanoparticle prepared by different methods and their

assemblies were taken by CE 7500 Dual BEAM UV-visible spectrophotometer. For this purpose deionized water was used to set the base line. The gold nanoparticles were washed carefully to eliminate the unwanted reactants and other materials which may interfere during UV-Visible scanning and dispersed in fresh deionized water. The washed gold nanoparticles were then taken in the spectrophotometer cell and deionized water was taken in reference cell. The sample cell was placed in spectrophotometer and scanned for λ_{max} from 350-900 nm.

Electron microscopy of nanoparticles: To further confirm the morphology (size and shape), gold nanoparticles and their assemblies prepared by different methods were characterized by Field Emission Scanning Electron Microscopy with Transmission Electron Detector (JEOL JSM 7500). For investigation a carbon coated copper grid having a diameter of approximately 3 mm was used. Samples were made by slow evaporation of one drop of dilute aqueous solution of the nanoparticles at room temperature for 3 h on to the carbon coated grid. These grids were then analyzed with FESEM.

RESULTS AND DISCUSSION

Gold nanoparticles by seed growth method: In the seeding growth methods, the growth of small particles (seeds) into larger particles was done. The seeds were used to create gold nanoparticles of different size. In this method we used seeds to grow step by step gold nanoparticles of different sizes. To synthesize gold nanoparticles of about 3.5 nm gold solution was reduced by sodium citrate. These were then used as seeds to synthesize the gold nanoparticles of about 5-10 nm. The UV-visible spectrum of these seeds is shown in Fig. 1. It showed the maximum plasmon band at 512 nm. As a mild reducing agent as corbic acid was used. It was added to the growth solution containing gold precursor and CTAB (Capping Agent). In order to synthesize different size of gold nanoparticles growth solution was shifted to four different flasks designated as A-D. At first the seeds were added to the A. The remaining B, C and D were prepared by step wise shifting of gold nanoparticles from the A to B, then B to C and finally from C to D. The UV-visible spectra for gold nanoparticles A, B, C and D showed the maximum plasmon band at 524, 524, 530 and 539 nm, respectively as given in Fig. 2-5.

Different size gold nanoparticles were prepared using step by step seeding growth method. This method elaborates the growth of small size particles into larger particles. The seeds synthesized in this study were sharp red in color having maximum Plasmon band at 512 nm as determined by UV-visible spectrophotometer. The color of gold nanoparticles solution A was wine red. Its maximum plasmon band was shifted from 512-524 nm in

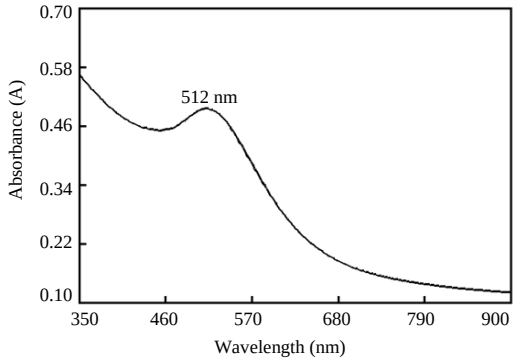

Fig. 1: UV-visible spectrum of gold nanoparticles used as seeds

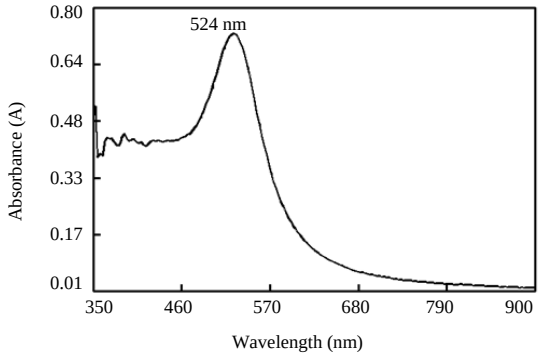

Fig. 2: UV-visible spectrum of gold nanoparticles (A)

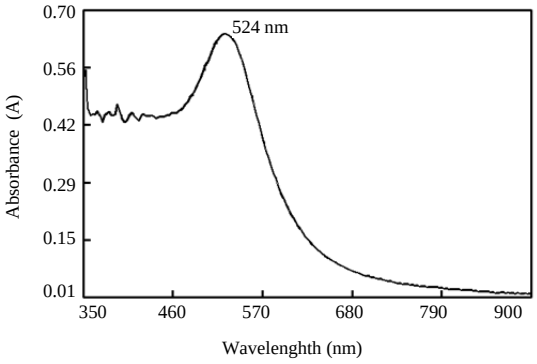

Fig. 3: UV-visible spectrum of gold nanoparticles (B)

the first step as A. Similarly the gold nanoparticles prepared in the second step (B) were deep red in color. Its maximum Plasmon band was obtained at 524 nm. Similarly the color of gold nanoparticles obtained by the next step of seeding growth, named as C was purplish pink. The UV-visible spectrum showed the maximum Plasmon band at 530 nm. The color of gold nanoparticles attained by last step of seeding growth was brown and the maximum plasmon band was attained at 539 nm. It was observed that the surface plasmon resonance band was

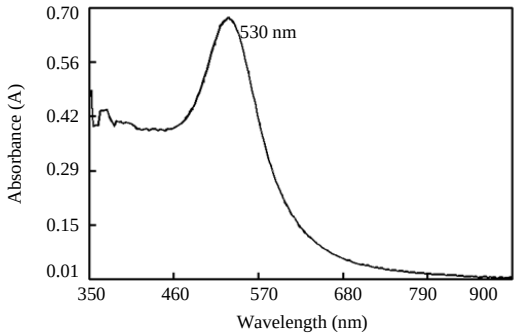

Fig. 4: UV-visible spectrum of gold nanoparticles (C)

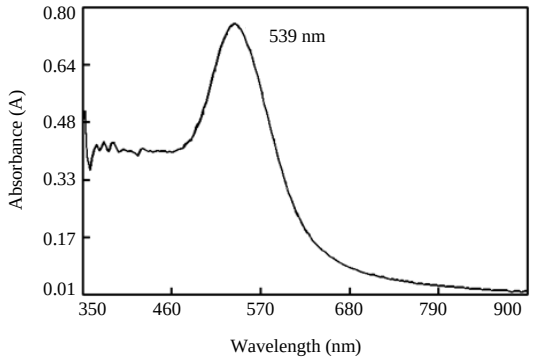

Fig. 5: UV-visible spectrum of gold nanoparticles (D)

shifted from 512-539 nm with increase in the nanoparticles size in the seeding growth method. Similar results were also observed by Jana *et al*.[23].

Gold nanoparticles A, B and C, synthesized by three different steps in seeding growth method were then investigated by FESEM/TEM in order to determine their size and shape. The results are shown in Fig. 6 and 7.

The size of gold nanoparticles confirmed by electron microscopic studies also presented the increase in size from A to D samples. The results showed 5-10 nm spherical gold nanoparticles in A, 15-20 nm spherical and triangle shape gold nanoparticles in B, 17-20 nm spherical nanoparticles in C and 50-60 nm nanoparticles in D.

Gold nanoparticles by citrate reduction method: In order to synthesize citrate stabilized gold nanoparticles, trisodium citrate was used. It act as reducing agent and also electrostatically stabilize the gold nanoparticles. The UV-visible spectrum for gold nanoparticles by citrate reduction method showed the maximum plasmon band at 521 nm as shown in Fig. 8.

The gold nanoparticles prepared by citrate reduction method were of ruby red color and UV-visible spectrum showed the maximum plasmon band at 521 nm. Kimling *et al*.[24] also observed the SPR at 520 nm

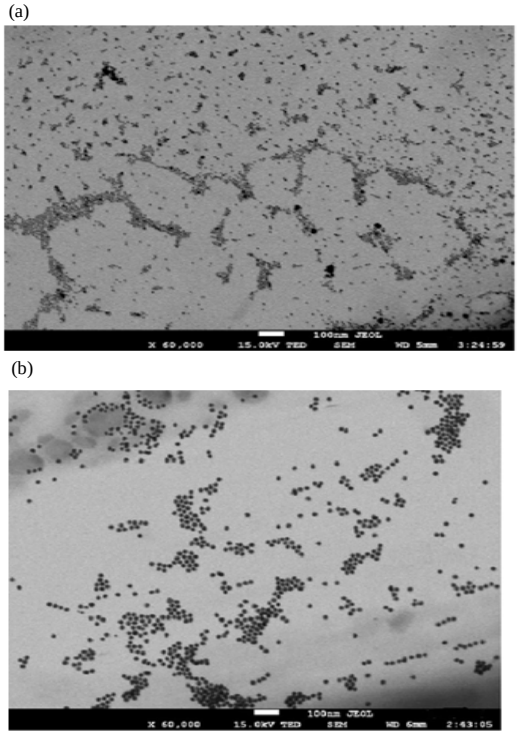

Fig. 6(a, b): (a) TEM micrograph of gold nanoparticles A and (b), TEM micrograph of gold nanoparticels B

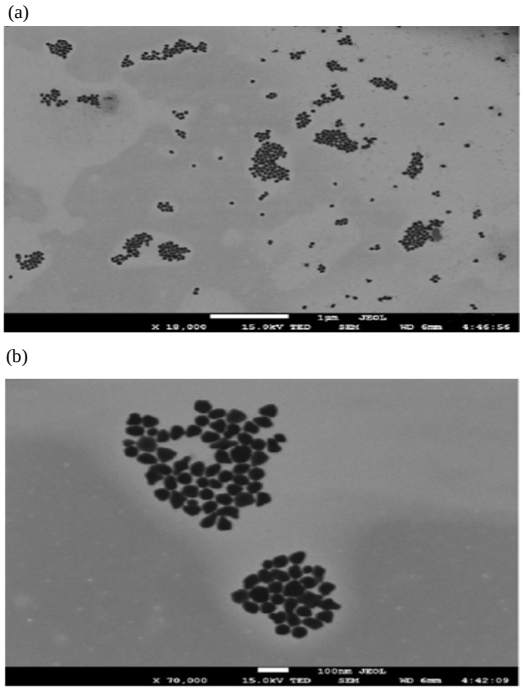

Fig. 7(a, b): (a) TEM micrograph of gold nanoparticles C and (b): TEM micrograph of gold nanoparticles D

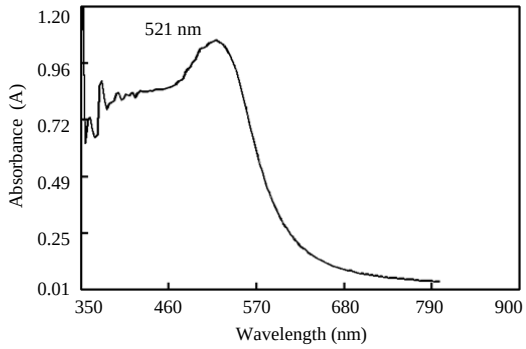

Fig. 8: UV-visible spectrum of citrate stabilized gold nanoparticles

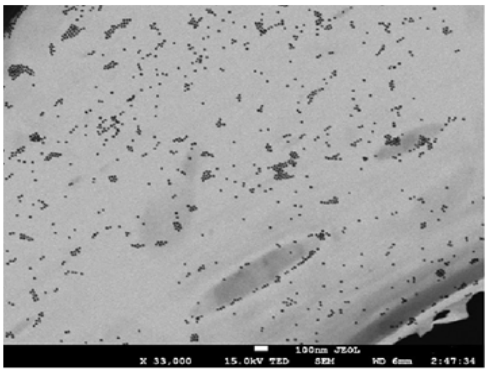

Fig. 9: FESEM micrograph of citrate stabilized gold nanoparticles

for the gold nanoparticles synthesized by reduction with citrate and ascorbic acid. FESEM characterization of these nanoparticles is shown in Fig. 9. FESEM characterization of these nanoparticles showed the formation of spherical ~15-20 nm gold nanoparticles as shown in Fig. 9.

Gold nanoparticles by sodium borohydride: The stability of gold nanoparticles synthesized by borohydride reduction method was further improved with sodium acrylate. The nanoparticles were refluxed with sodium acrylate to get more stable gold nanoparticles. The UV-visible spectrum of gold nanoparticles before and after reflux showed the maximum plasmon band at 514 nm and 520 nm, respectively as shown below in Fig. 10.

The UV-Visible spectra in Fig. 11 showed that the reflux process has increased the absorbance of gold nanoparticles. This was accompanied with an increase in maximum plasmon band from 514-520 nm for both before and after the reflux process. Gold nanoparticles prepared by sodium borohydride reduction method were analyzed using FESEM. The results are shown in Fig. 11.

The results of Fig. 11 showed the formation of spherical gold nanoparticles of about 10-12 nm. These nanoparticles were also analyzed using TEM

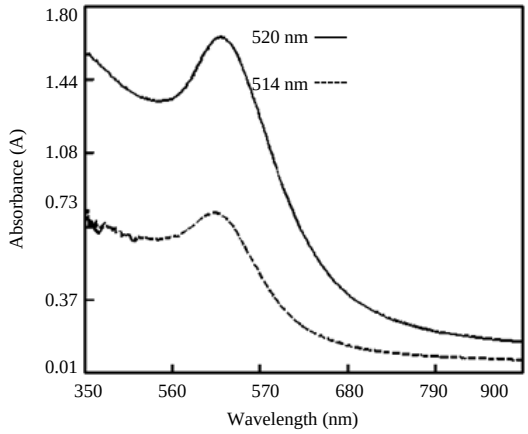

Fig. 10: UV-visible spectra of gold nanoparticles before and after reflux

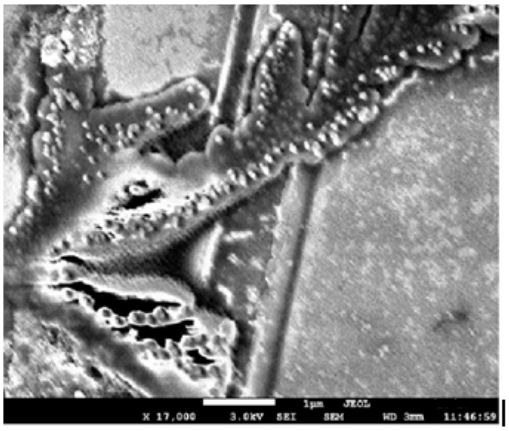

Fig. 11: FESEM micrograph of gold nanoparticles synthesized by borohydride reduction method

and the results (Fig. 13) clearly indicate the formation of spherical gold nanoparticles of about 10-12 nm.

Combination of gold nanoparticles with ethanol and 1, 9-nonanedithiol: The concentrated pellets of gold nanoparticles synthesized by sodium borohydide reduction and refluxed with sodium acrylate were then re-dispersed in 0, 10, 20, 30, 50, 60, 80 and 90% ethanol/water (v/v) mixtures. The gold nanoparticles (200 μL) solution from each of the above stated ethanol/water mixtures was placed in each of the 96-well micro titer plate as shown in Fig. 13. The ratio of ethanol was enhanced from zero (pure deionized water) to 90% down the rows (i.e., 0, 10, 20, 30, 50, 60, 80 and 90% ethanol in water were used as the dispersion media in rows 1, 2, 3, 4, 5, 6, 7 and 8, respectively). The quantity of 100 μM NDT was enhanced along the column from left

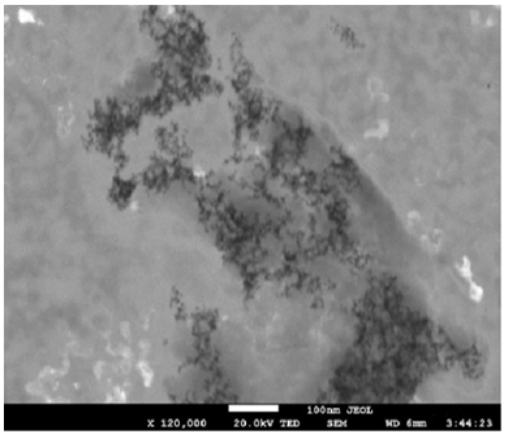

Fig. 12: TEM micrograph of gold nanoparticles

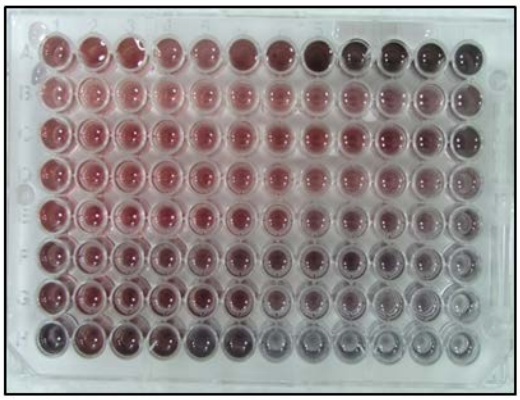

Fig. 13: An optical image of a 96-well microtiter plate

to right. It was increased as 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 μL of NDT and ethanol solution. It was added to the each well in columns 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12, respectively. For the control experiment, no NDT was added to the column 1well. By the adding the required volume of the ethanol/water mixture, the volume of reactant mixture in each well was made up to 300 μL. The reaction was supervised by taking the UV-visible spectra of each reaction after 24 h.

The results showed that the gold nanoparticles stabilized by acrylate were stable in 90% ethanol/water mixtures. It was evident that no change in color was observed. The UV-visible spectra of the gold nanoparticle solution of the microtiter plate are shown in Fig. 14. Interestingly, in the wells at the bottom row (H_1-H_6) of the microtiter plate, a regular change in color from red to purple and then to bluish purple was observed. It was observed in the wells where 90% ethanol/water mixture was used. The results showed that as the concentration of NDT increases the aggregation becomes more prominent as indicated by color change from red to blue. The UV-

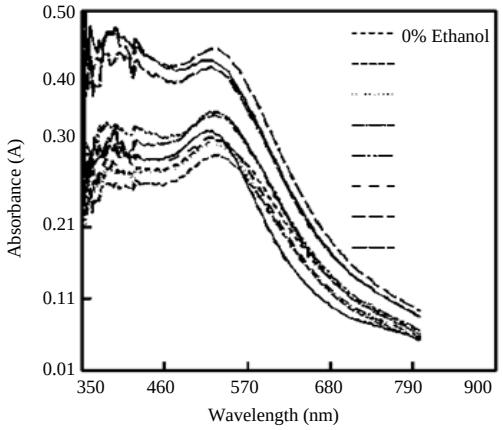

Fig. 14: UV-visible spectra of gold nanoparticles for 0% ethanol/water mixture for different concentration of NDT

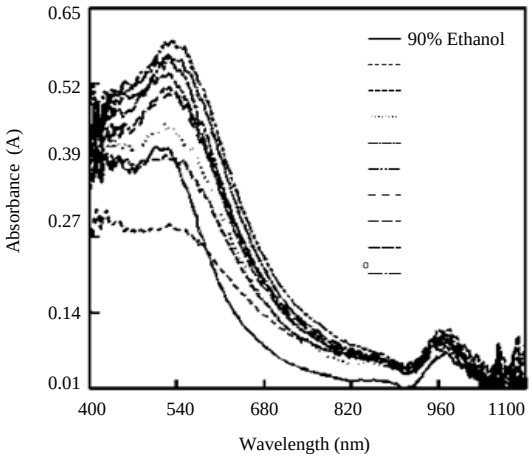

Fig. 15: UV-visible spectra of gold nanoparticles 90% ethanol/water mixture for different concentration of NDT

visible spectra for 0 and 90% ethanol/water mixture and different concentrations of NDT are shown in Fig. 14 and 15, respectively.

The results showed that there is no 2nd peak appeared in the UV-visible spectra of 0% ethanol/water mixture for different concentration of NDT. However, a second peak at 90% ethanol/water mixture containing different concentration of NDT is appeared at 950 nm. Their aggregation with NDT increases with increases in the concentration of NDT and in some cases, results in complete precipitation of gold nanoparticles.

CONCLUSION

The synthesis, morphology and stability of gold nanoparticles were studied in this research work. Gold

nanoparticles were synthesized by seed growth method, citrate-reduction method and from sodium borohydride and then refluxed with sodium acrylate. These nanoparticles were then characterized using UV-visible visible spectrophotometer, Transmission Electron Microscope (TEM) and Field Emission Scanning Electron Microscope (FESEM). In the seed growth method gold nanoparticles were synthesized by four steps of seeding growth showed maximum plasmon bands at 524, 524, 530 and 539 nm as investigated by UV-visible spectrophotometer. The TEM micrograph showed that gold nanoparticles attained from first step of seeding were spherical with diameter of about 5-10 nm, second step gold nanoparticles were spherical and triangle shaped with diameter of about 15-20 nm. Whereas gold nanoparticles attained from third and fourth step of seeding were spherical with17-20 and 50-60 nm size, respectively. The gold nanoparticles synthesized by sodium borohydride were then checked for their controlled aggregation in 1, 9-Nonanedithiol (NDT). The UV-visible spectra clearly showed the appearance of second plasmon resonance band at 950 nm that rises in intensity with the increase in NDT concentration. It is cleared in the UV-visible spectra for 80 and 90% ethanol/water mixtures and different concentrations of NDT in gold nanoparticles.

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