

The effect of silica concentrations on the absorbance of gold nanoparticles

Zakariya Yahia*, Raad M. S. Al-Haddad

Department of Physics, College of Science, Baghdad of University, Baghdad-Iraq

Abstract : The study showed the effect of different concentrations of silica by varying the volume of silica source (sodium silicate stock solution) on the absorbance of surface plasmonic resonance (SPR) of coated gold nanoparticles (AuNPs) using UV-visible spectrophotometer. The absorbance of AuNPs without coating at wavelength 521nm and 522nm with coating. The absorbance is increased by increasing the concentration of Silica and reached to optimum value at volume 0.5ml of sodium silicate stock solution and then decreased although the concentration of Silica increased. Gold nanoparticles is synthesized chemically from the solutions of Chloroauric acid (HAuCl_4) and Trisodium citrate dihydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) as a reducing agent using Turkevich method, then it coated with sodium silicate stock solution (Na_2SiO_3).

Keywords : Silica, AuNPs, absorbance, Turkevich method, surface plasmonic resonance, reducing agent, Chloroauric acid.

Introduction:

In the treatment of cancer tumors the silica which coated Gold nanoparticles (AuNPs) used as a characteristic in preventing Gold nanoparticles from deformation during heating by photothermal therapy. Nanotechnology is rapidly used in all fields of science and technology such as medical, dental, and electronic [1]. Colloidal gold nanoparticles (AuNPs) is used for several applications in biotechnology for their unique physical and chemical properties [2] as compared to their bulk materials due to : first the quantum size effect and second to the large reactive and exposed surface area, as a result of the specific electronic structures [3], where the oscillation of the free electrons in conduction band induced by an interacting electromagnetic field. These resonances known as surface plasmons [4]. Many different methods is synthesized and developed to generate gold nanoparticles (AuNPs). One of them is The chemical methods [2] [3] and Turkevich method is one of chemical preparation performed the first structural studies of Gold nanoparticles by electron microscopy, and Frens23 developed the work and showed the possibility to tune the size of AuNPs from ~ 16 to ~ 150 nm [5]. Gold nanoparticles (AuNPs) were prepared of distilled water on a hot plate stirrer, Chloroauric acid (HAuCl_4) was added to the distilled water and heated to boiling point and then the reducer and the stabilizer agent sodium citrate solution ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) was quickly added and stirred until the color turned to wine red [5] [6] [7]. The optical property of gold nanoparticles is changed due to the change in nanoparticles size [8]. This leads to a strong extinction band in the visible spectral region around 520 nm and a brilliant red color of the nanogold solution known as Surface Plasmon Resonance (SPR) [9], then Gold nanoparticles is coated by silica to prevent them from Aggregation [10] and from deforming when they heated up [11]. Controlled the thickness of silica caused tunable SPR effects [12]. Atomic Absorption Spectrophotometer (AAS) is a technique for measuring concentration (quantities) of chemical elements, based on measuring the absorbed radiation when

their bonds are broken (atomized). The concentration of element is directly proportional to the Absorbance and its value based on the Beer-Lambert law [13].

Experimental Method

Synthesis of Gold nanoparticles at room temperature :

To prepare 50ml of colloidal Chloroauric acid (HAuCl_4), add 0.15ml from 2% of Chloroauric acid solution (stock solution) to the 49.85ml of distilled water. Heating it at 100°C on hot plate without stirring till the solution starts an evaporation, stir the solution by magnetic bar and then add 0.5ml from 1% Trisodium citrate dihydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) solution (stock solution) at once and keep heating it until the color turned to wine red, cool the Gold nanoparticles solution at room temperature and then wash the solution by centrifuge device three times at 13000 rpm.

Coating gold nanoparticles by silica at room temperature :

To prepare 20ml of stock silica solution, add 0.3ml of Sodium silicate stock solution (26.5% and 10% Na_2O) to 19.7ml of distilled water. Add 4 drops from 8% of NaOH stock solution to get the pH of silica stock solution between 11 and 12 ($11 < \text{pH} < 12$) then add 1ml of this solution to 20ml of Gold nanoparticles solution and stir about 10 minutes. Store the above solution in dark place a whole night, then add 10ml of ethanol (purity 99%) to it and store it again in a same condition a whole night. Repeat the whole method by varying the volume of Sodium silicate stock solution (26.5% and 10% Na_2O) with 0.4ml, 0.5ml, and 0.6ml.

Results and Discussion

After synthesizing the Gold nanoparticles, the concentration is measured by Atomic Absorption Spectrophotometer (AAS) using wavelength $\lambda = 242.8\text{nm}$ for Gold and 4 samples of known concentrations for calibration (3.5 $\mu\text{g}/\text{ml}$, 7 $\mu\text{g}/\text{ml}$, 10.5 $\mu\text{g}/\text{ml}$, and 14 $\mu\text{g}/\text{ml}$). Fig. 1 shows the concentration of prepared AuNPs is 0.596 $\mu\text{g}/\text{ml}$

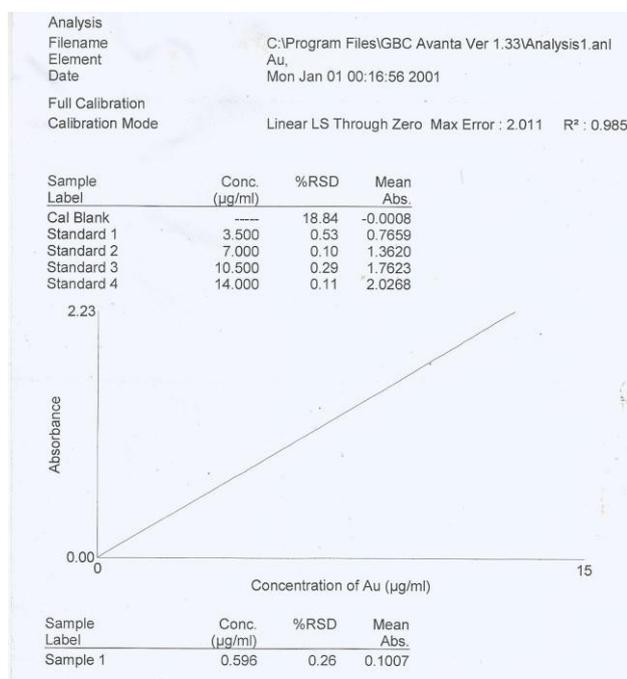


Fig 1 : the concentration of AuNPs is 0596 $\mu\text{g}/\text{ml}$, $\lambda = 242.8\text{nm}$

The UV-visible spectroscopy is used to measure the absorbance of AuNPs before and after the coating with 4 different volume of Sodium silicate stock solution (0.3ml, 0.4ml, 0.5ml, and 0.6ml). Fig. 2 shows the absorbance of surface plasmon resonance of gold nanoparticles at wavelength 521nm.

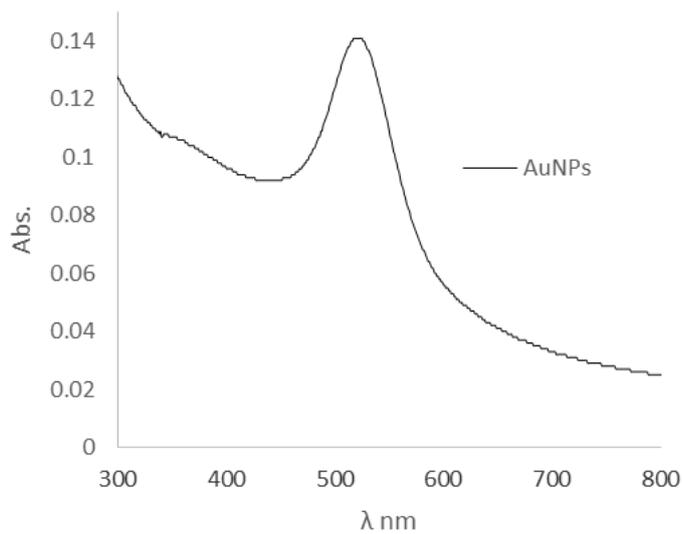


Fig 2 The absorbance of surface plasmon resonance of gold nanoparticles at $\lambda=521\text{nm}$.

And after coating the wavelength of the absorbance for four volumes of Sodium silicate stock solutions are at 522nm and the UV-visible spectrophotometer shows the effect of varying volumes, a red shift occurred to the SPR of AuNPs after coating which indicates to an agglomeration to the nanoparticles of gold and their size increased [7] [12], see fig. 3.

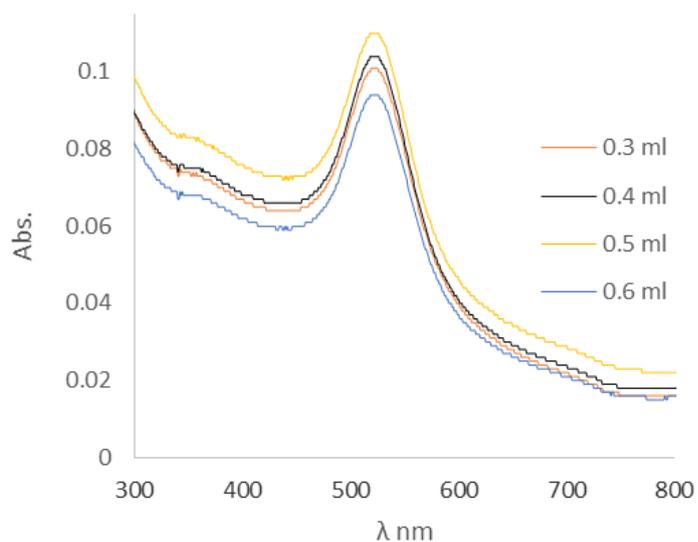


Fig. 3 The absorbance of surface plasmon resonance of coated gold nanoparticles with varying the volume of sodium silicate stock solution, $\lambda = 522\text{nm}$.

In fig. 4 the absorbance of SPR of AuNPs is increased by increasing the volume of sodium silicate stock solution and reached to the optimum value at 0.5ml and then decreased despite the volume increased which indicates the silica reached optimum value and not allowed the whole electromagnetic waves pass through it to gold nanoparticles.

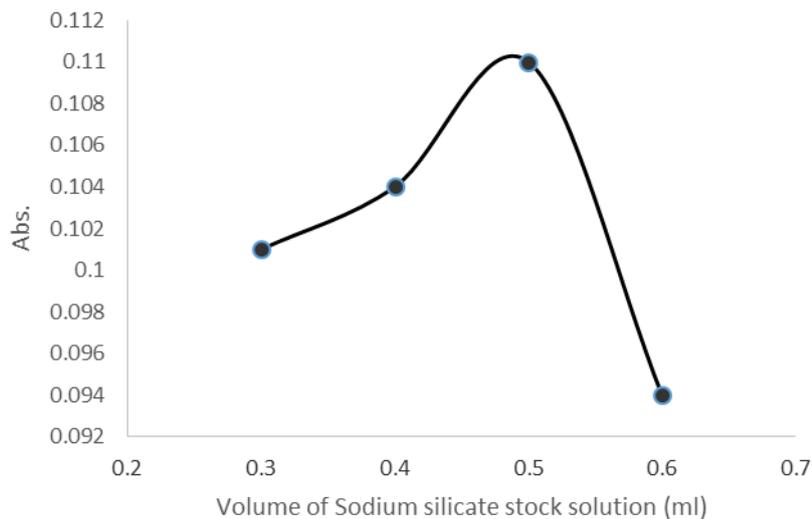


Fig. 4 The graph shows the effect of silica concentration on SPR of AuNPs.

By using AFM which measure the average diameter of AuNps before and after coating can give an explanation to the change in the absorbance of SPR see figure 5a-e

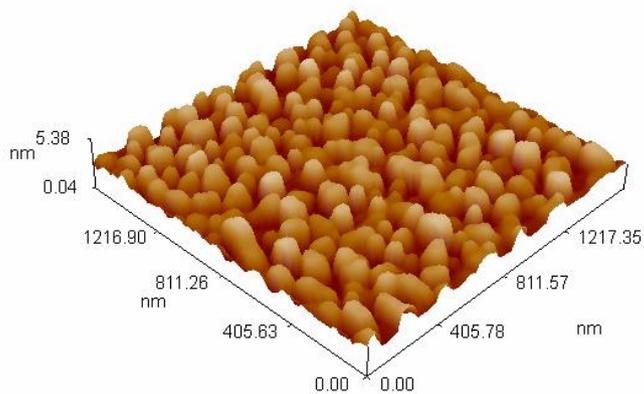


Fig 5–a AuNps before coating, Avg. Diameter:73.74 nm

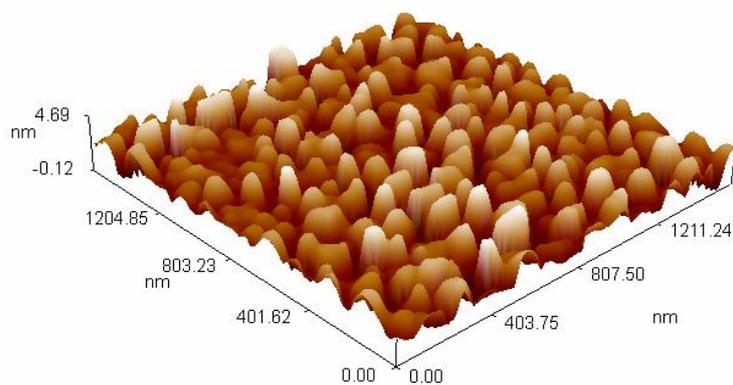


Fig 5-b AuNps coated with 0.3ml of stock silica, Avg. Diameter:77.29 nm

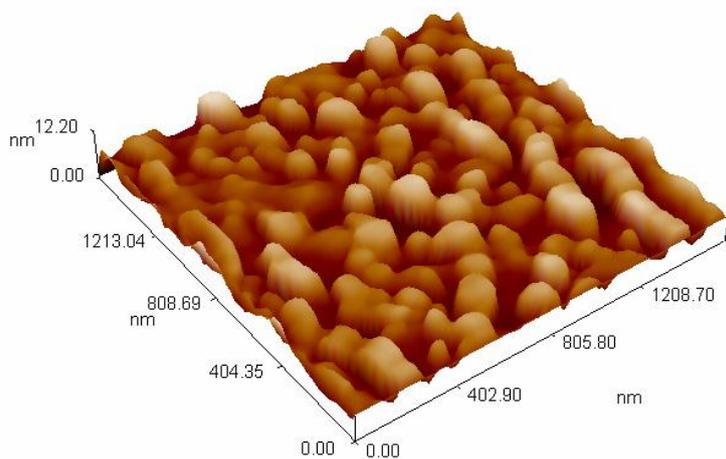


Fig 5-c AuNps coated with 0.4ml of stock silica, Avg. Diameter:95.43 nm

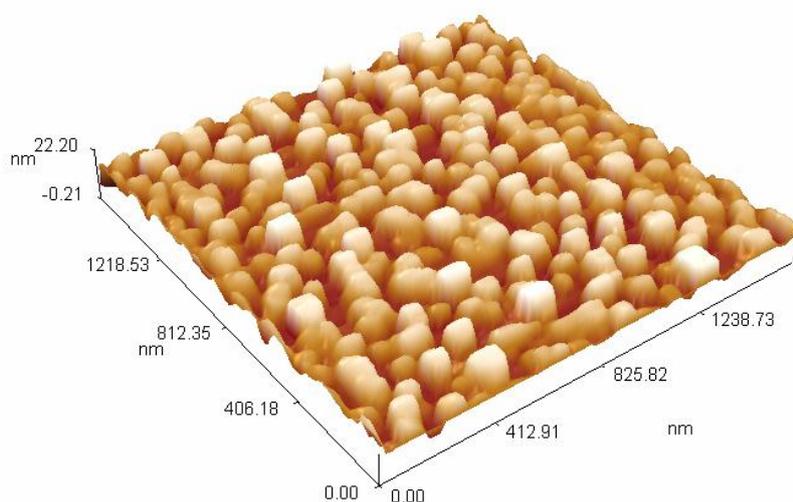


Fig 5–d AuNps coated with 0.5ml of stock silica, Avg. Diameter:97.27 nm

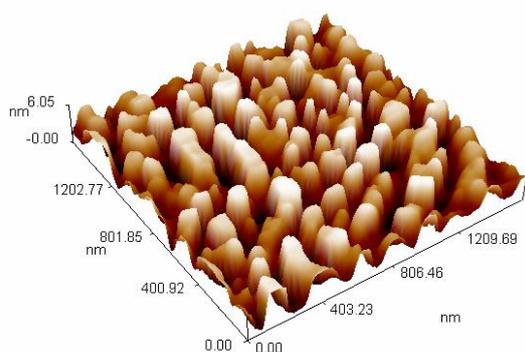


Fig 5–e AuNps coated with 0.6ml of stock silica, Avg. Diameter: 101.40 nm

In general, a coating with silica has a direct effect in varying the absorbance of surface plasmonic surface (SPR) of Gold nanoparticles by varying the volume of Sodium silicate stock solution (26.5% and 10%Na₂O) and reached to optimum value at 0.5ml. From fig. 1 and 2 a red shift occurred to the SPR of AuNPs from $\lambda = 521\text{nm}$ to 522nm respectively and the SPR wavelength of coated AuNPs is not changed although the volume of sodium silicate solution varied, which means the size of coated AuNPs is not changed, too. AFM shows an increasing in the average diameter of coated gold nanoparticles by increasing the volume of Sodium silicate stock solution and reach to the optimum value at 0.5ml and then decreased at 0.6ml which explains the changing in average diameter is not occurred to the size of gold nanoparticles but to the thickness of silica coating AuNPs see fig 6.

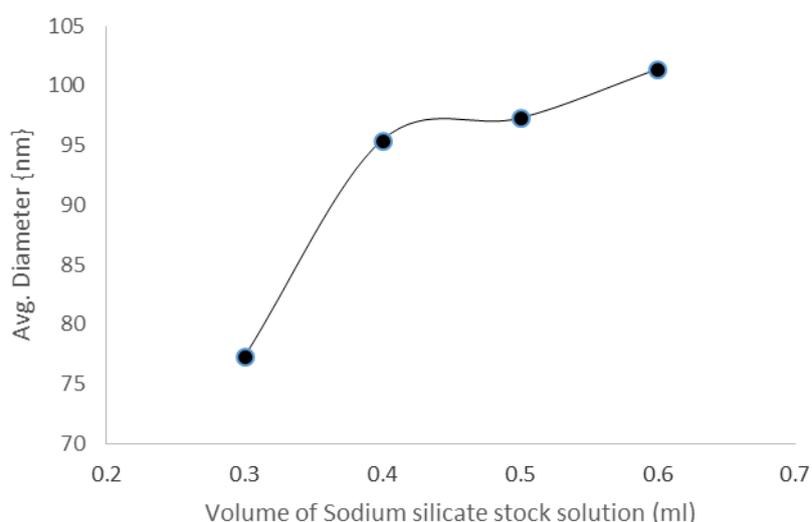


Fig. 6 Shows the average diameter of AuNPs directly proportional to volume of sodium silicate solution

Conclusion

The concentration of Silica has an effect on size and optical property of Gold nanoparticles, a red shift in SPR is occurred and the size increased. The thickness of silica coated AuNPs is increased by increasing the volume of sodium silicate solution and affect in the absorbance of surface plasmon resonance of gold nanoparticles. The absorbance is directly proportional to the increase in the volume of sodium silicate solution till reach to the optimum value (0.5ml) and then inversely proportional.

References

1. Ismail Ab Rahman, Vejayakumaran Padavettan, "Synthesis of Silica Nanoparticles by Sol-Gel Size-Dependent Properties, Surface Modification, and Applications in Silica-Polymer Nanocomposites—A Review", *Journal of Nanomaterials*, vol. 2012, article ID 132424, 2012.
2. Shah M., Badwaik V., "Gold nanoparticles: various methods of synthesis and antibacterial applications", *Frontiers in Bioscience* 19, pp. 1320-1344, June 1 2014.
3. AK Khan, R Rashid, G Murtaza and A Zahra, "Gold Nanoparticles Synthesis and Applications in Drug Delivery", *Tropical Journal of Pharmaceutical Research*, vol. 13, no.7, pp. 1169-1177, July 2014.
4. Stephan Link, Mostafa A. El-Sayed, "Size and Temperature Dependence of the Plasmon Absorption of Colloidal Gold Nanoparticles", *J. Phys. Chem. B*, 103, pp. 4212-4217, 1999.
5. Lorena García Fernández thesis, "Introducing Gold nanoparticle bioconjugates", Ph.D., Departament de Bioquímica i Biologia Molecular, Universitat Autònoma de Barcelona, 2013.
6. Soheila Honary, Pouneh Ebrahimi, Maedeh Ghasemitabar, "Preparation of Gold Nanoparticles for Biomedical Applications Using Chemometric Technique", *Tropical Journal of Pharmaceutical Research*, vol. 12, no.3, pp. 295-298, June 2013.
7. Susie Eustis, Mostafa A. El-Sayed, "Why gold nanoparticles are more precious than pretty gold: Noble metal surface plasmon resonance and its enhancement of the radiative and nonradiative properties of nanocrystals of different shapes", *Chemical Society Reviews*, DOI: 10.1039/b514191e, 22nd November 2005.
8. Stephan Link, Mostafa A. El-Sayed, "Shape and size dependence of radiative, non-radiative and photothermal properties of gold nanocrystals", *Int. Reviews Physical Chemistry*, vol. 19, no. 3, pp. 409-453, 2000.
9. Xiaohua Huang, Mostafa A. El-Sayed, "Plasmonic photo-thermal therapy (PPTT)", *Alexandria Journal of Medicine*, vol. 47, pp. 1-9, 2011.
10. Meera Basa thesis, "Synthesis & Characterization of Silica Coated Iron oxide Nanoparticles by Sol-Gel Technique", M.Sc., National institute of technology, Rourkela, Deemed University, May 2009.

11. Sotiris Pratsinis, "Hot nanoparticles for cancer treatments", *phys.org*, March 24, 2014.
12. Dong Kee Yi, "Au/Silica/Fe₂O₃ Nanohybrid Preparation and Biosensor Application", *Bull. Korean Chem. Soc.*, vol. 34, no. 5, 2013.
13. R. García, A. P. Báez, "Atomic Absorption Spectrometry (AAS)", Publisher *InTech*, 2012.
