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Z-scan Technique for Measurements of Glucose Concentrations through the Formation of Plasmonic Gold Nanoparticles Prepared by Green Synthesis

F. Abdulwahab[1], F. Z. Henari[2]

[1, 2]Department of Medical Sciences, Royal College of Surgeons in Ireland, Medical University of Bahrain, Building 2441, Road 2835, Block 228, Busaiteen, Kingdom of Bahrain

Abstract: ***Gold nanoparticles were synthesized by microwave irradiation using glucose as a reducing and stabilizing agent. The effects of using different concentrations of glucose in the synthesis of nanoparticles were investigated. The formation of gold nanoparticles was confirmed using UV-Vis absorption spectra and Transmission Electron Microscope(TEM). Z-scan technique was used to measure the nonlinear refraction indices of the gold nanoparticlessynthesized with different glucose concentrations. A linear relationship was found between the nonlinear refractive index of the total gold-glucose and concentration. Thus the calculated values of the nonlinear refractive index may be used for measuring an unknown glucose concentration in a sample.***

Keywords: gold nanoparticles, green synthesis, microwave, absorption spectra, nonlinear properties, Z-scan

1. Introduction

In recent years, there has been huge interest in research on metal nanoparticles due to their potential applications in the field photonics, optoelectronics such as sensors (1), and in medical applications such as diagnosis, drug delivery and cancer treatments (2–5).Recently, research has focused on green synthesis nanoparticles using plants and carbohydrate as a reduction agent and stabilizer (6,7). In the preparation of Au nanoparticles,glucose has been considered as one kind of reducing and capping agent(8),which plays an important role in preventing agglomeration and in controlling the formation of nanoparticles and their stability. Chemical methods are also used to synthesize gold nanoparticles(9). The synthesis of gold nanoparticles using microwaveheating has been reported (10).

Metal nanoparticles have a surface plasmon resonance (SPR) absorption in the visible region, which arises from collection motion of free electrons in the conduction band. The presence of SPR band enhances the nonlinear optical properties. These properties have a crucial role in development of optical limiting devices and optical switches. Applications with these nanoparticles can be used in detection of glucose level in blood(11).

Glucose is the main energy source for the human body. The concentration of blood glucose is regulated by several hormones, such as insulin and glucagon. The quantification of glucose in the blood is used for diagnosing metabolic disorders of carbohydrates, such as diabetes. Currently, the methodology used for this determination is the enzymatic colorimetric with spectrophotometric reading. Among other optical diagnostic methods, a nonlinear optical method is used for determining the changes in glucose level not detected by conventional methods. Determining glucose level using the nonlinear refractive index has been reported(12,13), where it has found a linear relationship between the measured nonlinear refractive index values and glucose concentration. One such method for measuring refractive index is the z-scan technique.

In this study, gold (Au) nanoparticleswere synthesized using glucose as a reduction agent and stabilizer under microwave heating. The nonlinear optical properties of Au nanoparticles combined with glucose were measured using the z-scan technique(14). Samples with different glucose concentrations were prepared. The formation of nanoparticles was monitored by measuring the UV-Vis absorption spectra. The maximum absorption band (SPR) was centered at 526 nm. The size distributions of synthesized nanoparticles were identified using Transmission Electron Microscopy (TEM).The z-scan experiment was performed using a 488 nm CW Argon-ion laser with a power of 29.2 mW. Effects of glucose concentration with embedded Au nanoparticles on the nonlinear refractive index were measured. The measurements showed a linear relationship between the glucose concentration and the nonlinear refractive index (n_2).

2. Experimental

2.1 Materials and methods

Gold chloride ($HAuCl_4$), sodium hydroxide (NaOH) and glucose ($C_6H_{12}O_6$) were purchased from Sigma Aldrich. Distilled water was used throughout the experiment, even for washing glassware.

2.2 Synthesis of gold nanoparticles

For the green synthesis of gold nanoparticles, in a test tube 68.4 µL of 1% wt. gelatin, 22.8 µL of 1 M NaOH, 454.6 µL of different concentrations of glucose and 454.6 µL of 10 mM $HAuCl_4$ were added, respectively. Then the test tube was heated in a microwave oven at low power for 30 seconds and was allowed to cool to room temperature for further analysis. Formation of gold nanoparticles was confirmed by the color change from colorless to red. In this reaction, glucose reduces gold chloride (Au^{+3}) to gold atoms

(Au^0), and acts as stabilizing and capping agent. Chemical equation is given below(15)

$$[AuCl_3(OH)]^{-}+C_6H_{12}O_6 \rightarrow Au^0+\text{products}$$

2.3 Characterization of the synthesized gold nanoparticles

Following the synthesis of nanoparticles, UV-Vis spectrometer (Shimadzu UV-1800) was used to record the absorption spectra of the gold nanoparticles to obtain information about the surface plasmon resonance band (SPR), and shapes of the nanoparticles. Transmission electron microscopy (TEM) was used to confirm the formation of nanoparticles and their shapes. Size distribution of nanoparticles was surveyedfrom the TEM images using ImageJ 1.5g software.

3. Results and Discussion

3.1 Absorption Spectra

The absorption spectra of gold nanoparticles synthesized with different glucose concentrations were recorded over range of 350 -800 nm with UV-Vis spectrometer using 10 mm quartz cuvette as shown in Fig.1. It is well known that the metal nanoparticles exhibit distinctive optical properties due to combined oscillation of conduction band electrons in resonance with the incident wavelength, which is known as the surface plasmon resonance (SPR) band. The UV-Vis absorption spectrum of gold nanoparticles is characterized by a surface plasmon resonance band centered at 526 nm, which is typical for gold nanoparticles. The sharp peaks indicate the formation of spherical nanoparticles, which was confirmed by TEM images of gold nanoparticles. There were no evident changes in the peak position over the range of concentrations used for this experiment except for the increase of the absorbance peak. The increase of the absorption peak demonstrates that the amount of gold particles increases. The stability of the SPR peak position indicates that the Au nanoparticles do not aggregate. In Fig.2 the graph shows a linear relationshipbetween the absorbance of gold nanoparticles surface plasmon resonance band and the glucose concentration.

The point at 800 nm was used as reference for determining the height of SPR peak. This graph may be used for the determination of the concentration of a sample fromthe absorbance peak.

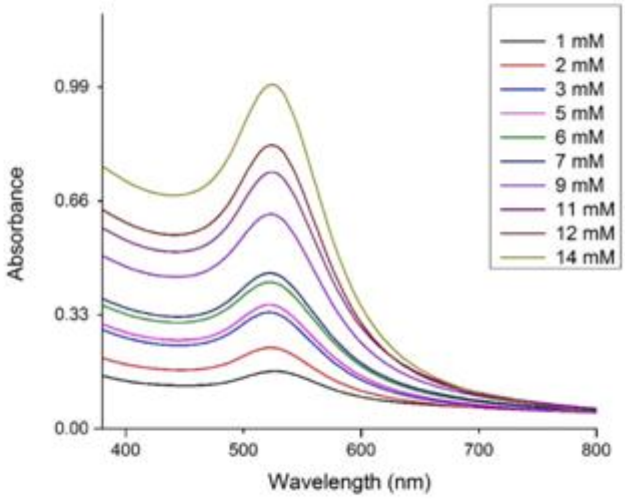

Figure 1: UV-Vis absorption spectra of gold nanoparticles synthesized using different glucose concentrations and gelatin.

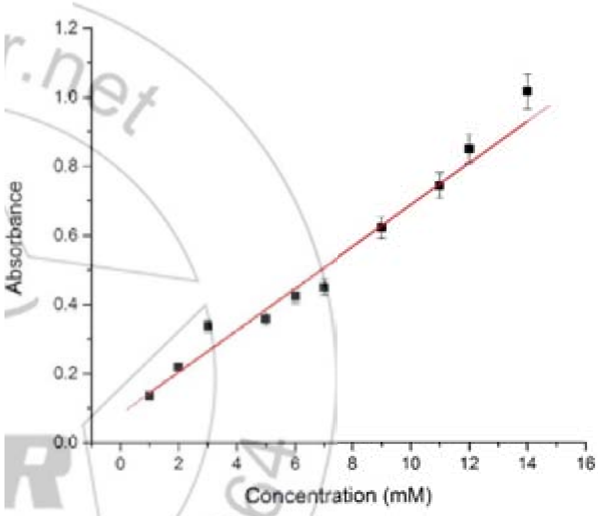

Figure 2: Variations in absorbance of gold nanoparticles synthesized using different glucose concentrations.

3.2 Transmission Electron Microscopy (TEM)

TEM images of gold nanoparticles synthesized using glucose 8 mM and 14 mM are shown in Fig. 3 & 4. The size distribution of nanoparticles was analyzed using ImageJ 1.5g software. This is performed by converting pixels on the TEM images into nanometers by applying the scale of the image. Polydisperse gold nanoparticles synthesized using 8 mM of glucose were observed and diameters were found to range from 3 – 28 nm with a high yield of size 3.7 nm. Polydisperse gold nanoparticles synthesized using 14 mM of glucose were observed, and diameters were found to range 8 – 22 nm with a high yield of size 9 nm. Larger nanoparticles were synthesized as the concentration of glucose increases. Shade observed around the gold nanoparticles is believed to be that of glucose.

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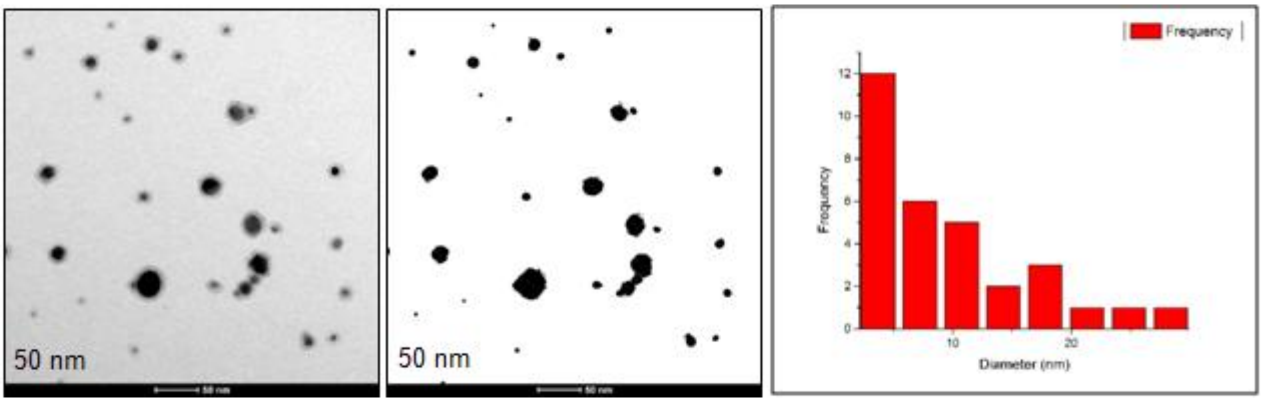

Figure 3: TEM image and corresponding size distribution histogram of gold nanoparticles synthesized using 8 mM glucose and gelatin

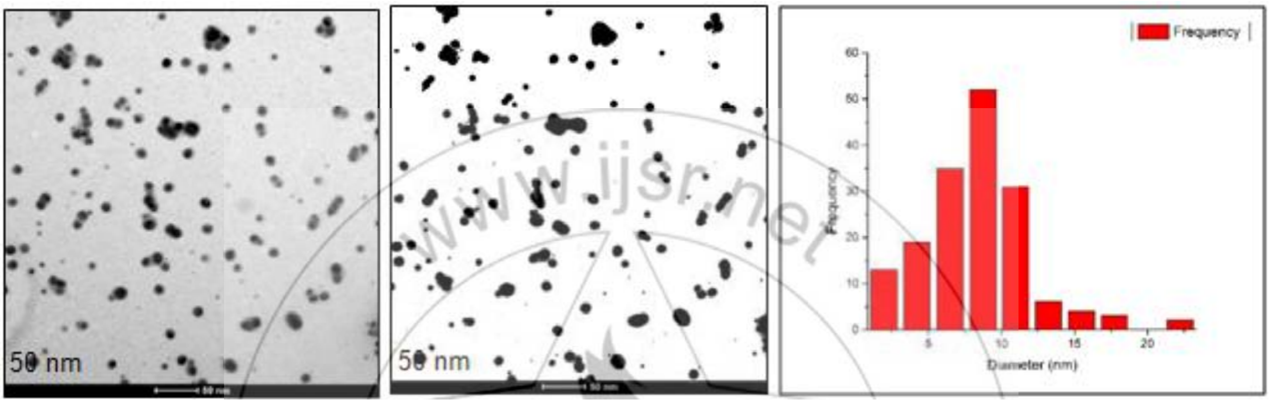

Figure 4: TEM image and corresponding size distribution histogram of gold nanoparticles synthesized using 14 mM glucose and gelatin

4. *Z*-scan measurements

The synthesized gold nanoparticles were subjected to the optical nonlinearity measurements using the z-scan technique. The experiment was performed with an air-cooled Argon-ion laser beam operating at 488 nm with a power of 29mW. The beam was focused to a beam waist of 20 μm with a lens of 10 cm focal length, giving a typical power density range of 4.78x10^{7} W/m^{2}. The transmission for the samples was measured with an aperture in the far-field of the lens as the samples moved through the focal point. The normalized transmittance curve is characterized by a prefocal peak followed by a postfocal valley [Fig. 5]. This implies that the nonlinear refractive index of gold nanoparticles synthesized with glucose is negative ($n_2 < 0$), (defocusing effect). The process leading to refractive index change, involves the excitation of the electrons from the SPR band. The excited electrons interact with the electric field of the incident beam leading to higher order oscillations. The excited hot electrons (electrons with higher energy than Fermi energy) are thermalized by dissipating the excess to the surroundings. The excess thermal energy increases the surrounding temperature and generates a temperature gradient. This temperature gradient leads to a variation in the refractive index, which is called a thermal lens (16).

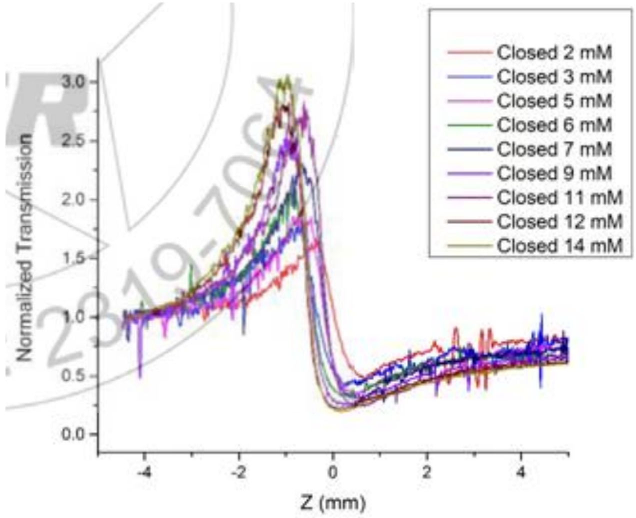

Figure 5: Closed aperture z-scan of gold nanoparticles synthesized using glucose and gelatin. Using CW argon-ion laser with λ=488 nm, Power=29.2 mW.

The nonlinear refractive index n_2 is calculated from thedifference of normalized peak to valley variation ($\Delta T_{p\text{-}v}$) of the measured transmittance. The difference between normalized peak–valley transmittance $\Delta T_{p\text{-}v}$ is given by

$$\Delta T_{p-v} = 0.406(1-S)^{0.25}|\Delta\phi| \tag{1}$$

where $\Delta|\phi|$ is the on axis nonlinear phase shift at the focus and S is the linear transmittance of the aperture and is given by

$$S = 1 - \exp(-2r_a^2 / w_a^2) \quad (2)$$

where r_a is the radius of the aperture and w_a is the radius of the laser at the entrance of the aperture. The nonlinear phase shift is given by

$$\Delta|\phi| = \frac{2PL_{eff}}{\lambda w_o^2} n_2 \quad (3)$$

where n_2 is the nonlinear refractive index, P is the laser power, λ is the laser wavelength and $L_{eff} = (1 - \exp(-\alpha L))/\alpha$ where α is the linear absorption coefficient at 488 nm, L is the sample thickness, L_{eff} is the effective thickness of the sample and w_o is the radius of the laser at the focus(17).

Equations 1 and 3 were used to calculate the value of the nonlinear refractive indexn_2. Fig.5 shows the results of a typical closed aperture z-scan for different glucose concentrations. Fig.6 shows the calculated values of n_2 for different concentrations of glucose. It showsa linear relationship between the nonlinear refractive indexand the glucose concentration. Hence, the nonlinear refractive index can be used for the determination of unknown glucose concentration in a sample.

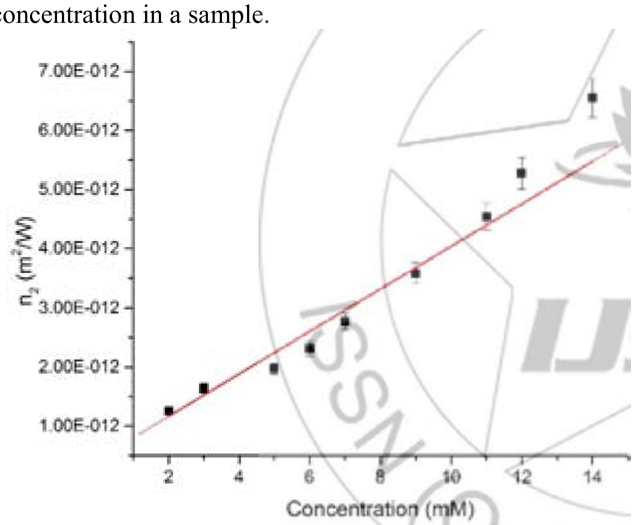

Figure 5: Variation in the nonlinear refractive index (n_2)for different glucose concentrations.

4.1 Comparison between glucose measurements using glucometer and z-scan technique

Standard solutions made with Au nanoparticles. The glucose concentrations were measured using a glucometer and compared with the measurements calculated from the z-scan technique results. As shown in Table 1, the results are in good agreement with those measured using glucometer, the error between the measurementsfor three different concentrationsdidn't exceed 6%.

Table 1: Concentration of glucose measured using glucometer, z-scan technique and the calculated percentage error

Glucose concentration using glucometer (mM)	*Glucose concentration using z-scan (mM)*	*% Error*
4.5	4.7	4.44 %
7.5	7.05	6 %
12.5	12.67	1.36 %

5. Conclusions

Green synthesis method was used to synthesis gold nanoparticles from soluble glucose, which acts as reduction and as stabilizing agent using microwave heating.UV-Vis absorption spectroscopy results confirmed formation of Au nanoparticles through SPR band, and the particle size distribution was determined using TEM. The effect of different glucose concentration on gold nanoparticles was investigated. Thez-scan technique was used to measure the nonlinear refractive index of gold nanoparticles at different glucose concentrations. The results were compared with measurements made using glucometer and found to be in good agreement. Therefore,the nonlinear refractive index values may be used for measuring the glucose concentration. Experiment is in progress to use the z-scan technique to determine glucose levels in biological samples.

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