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Full Length Research Paper

Dielectric constant, electrical conductivity and relaxation time measurements of different gold nanoparticle sizes

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Gold nanoparticles (GNPs) offer a great possibility for biomedical application, not only to pharmaceutics approaches, but also as novel diagnostic and therapeutic approaches. One of the important concerns is about their safety in clinical applications. Nanoparticle size has been shown to be an extremely important parameter affecting the nanoparticle uptake and cellular internalization. The aim of the present study was to investigate the dielectric constant, electrical conductivity and relaxation time of different GNP sizes. The electrical parameters were measured in the frequency range of 20 Hz up to 1 MHz using a WAYNE KERR precision component analyzer. The sample cell has two squared platinum black electrodes each having an area of 1 × 1 cm^2 with an inner electrode distance of 1 cm. For a dielectric material placed between two parallel plate capacitor, the measured value of capacitance (C) and resistance (R) were used to calculate the real (ε') and imaginary part (ε'') of the complex permittivity $\varepsilon^* = \varepsilon' - j\varepsilon''$, in addition to calculating the conductivity (σ) and the relaxation time (τ). The sizes of GNPs were calculated from the images taken by the transmission electron microscope (TEM). It became evident that relatively simple methods can be used to obtain the populations of different GNP sizes, which allow simultaneous detection of several targets. The presented dielectric data indicates that GNPs have strong dielectric dispersion corresponding to the alpha relaxation region in the frequency range of 20 Hz to 100 kHz which was identified as anomalous frequency dispersion. The measured conductivity values decreased with increasing GNPs size. Moreover, at high frequencies, the conductivity rapidly increased for all the examined GNPs size. The GNPs show a relaxation process. The relaxation time decreased with increasing GNPs size and was found to be 2.5, 3.5 and 4 ms for 10, 20 and 50 nm GNP size, respectively. A rapid decrease in the dielectric constant may be attributed to the tendency of dipoles in the GNPs to orient themselves in the direction of the applied field in the low-frequency range. However, in the high-frequency range, the dipoles will hardly be able to orient themselves in the direction of the applied field and hence, the value of the dielectric constant is nearly constant. The relaxation time may be attributed to increase in the localized charges distribution within the medium which was confirmed by the conductivity data. This study demonstrates that the dielectric, electrical conductivity and relaxation time values decreased with increasing the GNPs size, e.g. these changes are particle-size dependent. This study suggests that the increase in dielectric constant, electrical conductivity and relaxation time observed with the smaller 10 and 20 nm GNPs compared with 50 nm GNPs may be used as important risk factors for bioaccumulation and toxicity of the smaller GNPs. Thus additional histological and histochemical experiments are needed to confirm this hypothesis.

Key words: Gold nanoparticles, rheological parameters, size, temperature, dielectric, conductivity.

INTRODUCTION

The small sizes of nanoparticles (NPs) imply that they could get close to a biological target of interest; nanomaterials can be useful for both *in vivo* and *in vitro* biomedical research and applications. Therefore, an increased attention is focused on the applications of NPs in biology and medicine. Metallic NPs can be made to resonantly respond to a time-varying magnetic field, with advantageous results related to the transfer of energy to the particles (Caruthers et al., 2007; Pissuwan et al., 2006; Kogan et al., 2007) which can be used as a hyperthermic agent, thereby delivering toxic amounts of thermal energy to targeted bodies such as tumours' (El-Sayed et al., 2006a, b; Kogan et al., 2006; Zharov et al., 2006; Hirsch et al., 2003).

The GNPs shows several features that make them well suited for biomedical applications, including straight forward synthesis, stability and the ability to selectively incorporate with recognition molecules such as peptides or proteins (Pissuwan et al., 2006).

A study on nanoparticle is becoming a hot point owing to their novel physical and chemical attributes in electronics (Brust et al., 1998; Li and Jiang, 1997; Schmid, 1992; Brust et al., 1995), optics (Brust et al., 1998; Collier et al., 1997) and electro-magnetic (Sun et al., 2000).

The GNPs have unique optical properties, such as distinctive extinction bands in the visible region due to surface plasmon oscillation of free electrons (Schmidt, 1992).

The physical origin of the light absorption by GNPs is the coherent oscillation of the conduction band electrons induced by the interacting electromagnetic field. The absorption band results when the incident photon frequency is resonant with the collective oscillation of the conduction band electrons, and is known as the surface plasmon resonance (SPR). The resonance frequency of this SPR is strongly dependent upon the size, shape, dielectric properties and local environment of the NPs (Kreibig and Vollmer, 1995; Mirkin and Ratner, 1997). This is attributable to electric dipole-dipole interaction and coupling between plasmons of neighbouring particles in the dispersion.

SPR property allows the use of GNPs for many applications in the bioscience and medical fields. The GNPs are used as immunostaining marker particles for electron microscopy and as chromophores for immunoreactions and nucleic acid hybridization (Pissuwan et al., 2006). Their application for gene delivery into cells was reported (Sullivan et al., 2003; Sandhu et al., 2002).

In addition, GNPs have attracted much attention as photo-thermal agents in hyperthermia (El-Sayed et al., 2006a, b).

Owing to the unique optoelectronic properties with their controlled size and morphology, GNPs find significance in the field of bionanotechnology (Sperling et al., 2008) as biomarkers (Wan et al., 2008), biosensors (Tokonami et al., 2008) and cancer diagnostic (Huang et al., 2007).

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Over the past few years, the dielectric properties of different NPs have been extensively investigated to get attractive information about the localized surface plasmons and their local dielectric environment (Zhang et al., 2010; Scaldaferri et al., 2009).

The objective of the present experimental work is to explore the effects of GNP size on the electrical permittivity (ε'), conductivity (σ) and loss factor (tan δ) in the frequency range of 20 Hz to 100 kHz at the room temperature.

MATERIALS AND METHODS

Gold nanoparticles size

Different GNP sizes were purchased (Product MKN-Au, Canada) and used in this study. The GNP sizes were in aqueous solution of size 10 nm (Product MKN-Au-010; concentration 0.01% Au), GNPs of size 20 nm (Product MKN-Au-020; concentration 0.01% Au) and GNPs of size 50 nm (Product MKN-Au-050; concentration 0.01% Au).

Electrical parameters

The electrical parameters were measured in the frequency range of 20 Hz up to 1 MHz using a WAYNE KERR precision component analyzer, model 6440 B (UK). The sample cell has two squared platinum black electrodes each having an area of 1 × 1 cm^2 with an inner electrode distance of 1 cm. The measurements were performed at the room temperature. For a dielectric material placed between two parallel plate capacitor, the measured values of capacitance (C) and resistance (R) were used to calculate the real part (ε') and imaginary part (ε'') of the complex permittivity $\varepsilon^* = \varepsilon' - j\varepsilon''$, while conductivity (σ) and the relaxation time (τ) were calculated using the following equations:

1. $\varepsilon' = \varepsilon_0 C k \quad k = 1 cm^{-1}$ where k is the cell constant which depends on the cell dimensions
2. Loss tangent $\tan\delta = \varepsilon''/\varepsilon' = 1/2\pi fRC$ so, $\varepsilon'' = \varepsilon' \tan\delta$
3. The conductivity $\sigma = k / R \ (\Omega^{-1} m^{-1})$
4. Relaxation time $\tau = 1/2\pi f_c$, where f_c is the critical frequency corresponding to the mid point of the dispersion curve. If any dielectric material is introduced between the two plates, the corresponding response to a sinusoidal field will be characterized by dielectric properties (dielectric permittivity (ε) and conductivity (σ) which vary with frequency). The charge and current densities induced in response to an applied electric field is an example of an idealized parallel plate.

RESULTS AND DISCUSSION

Size and morphology of different gold nanoparticles

The 10 and 20 nm GNPs show spherical morphology while GNPs of 50 nm show hexagonal morphology. All

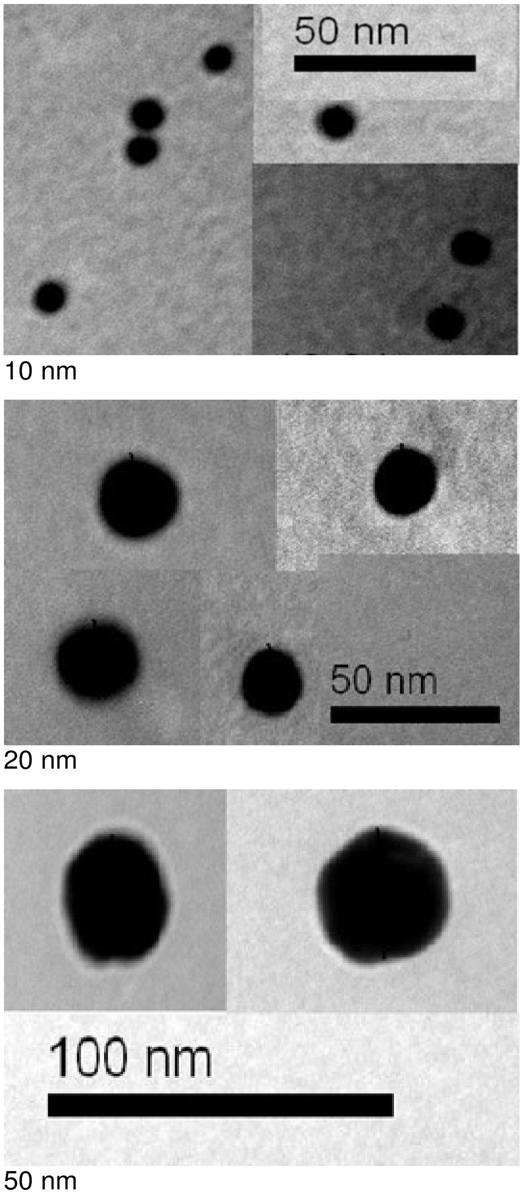

Figure 1. TEM images for different GNP samples.

GNPs were with good particle size distribution dispersed in the solution as shown in Figure 1.

The mean sizes for 10, 20 and 50 nm GNPs were calculated from the images taken by the transmission electron microscope (TEM). It became evident that relatively simple methods can be used to obtain populations of different GNP sizes, which allow simultaneous detection of several targets. The measured mean size for GNPs of size 10 nm was 9.45 ± 1.33 nm, for GNPs of size 20 nm was 20.18 ± 1.80 nm and was 50.73 ± 3.58 nm for GNPs of size 50 nm. The high electron densities of GNPs as well as the homogeneity of the particles shape and size make them highly conspicuous under the TEM (Abdelhalim, 2011).

The dielectric measurements

Figures 2 and 3 show the variation of electrical permittivity (ε') and conductivity (σ) with frequency at room temperature for 10, 20 and 50 nm GNPs. The presented dielectric data indicates that the GNPs have strong dielectric dispersion corresponding to the alpha relaxation region in the frequency range of 20 Hz to 100 kHz which was identified as anomalous frequency dispersion.

A rapid decrease in the dielectric constant may be attributed to the tendency of dipoles in the GNPs to orient themselves in the direction of the applied field in the low-frequency range. However, in the high-frequency range the dipoles will be hardly oriented in the direction of the applied field and hence, the value of the dielectric constant is nearly constant. The measured conductivity values increased with decreasing the GNPs size. Moreover, at high frequencies, the conductivity values rapidly increased for all the examined GNPs size.

The variation of loss factor ($\tan\delta$) as a function of frequency for 10, 20 and 50 nm GNPs is shown in Figure 4. It is clear that GNPs show a relaxation process. The relaxation time was found to decrease with the increase of GNPs size and was found to be 2.5, 3.5 and 4 ms for 10, 20 and 50 nm GNP size, respectively. This may be attributed to increasing the localized charges distribution within the medium which was confirmed by the conductivity data (Figure 3).

Further studies are requested to use the smaller GNPs size (10 and 20 nm) *in vivo* and *in vitro* to assess its bioaccumulation and toxicity in several tissues to confirm their risk effects**.**

Conclusions

The presented dielectric data indicates that the GNPs have strong dielectric dispersion corresponding to the alpha relaxation region in the frequency range of 20 Hz to 100 kHz which was identified as anomalous frequency dispersion.

The measured conductivity values increased with decreasing the GNPs size. Moreover, at high frequencies, the conductivity rapidly increased for all the examined GNPs size.

The GNPs show a relaxation process. The relaxation time was found to decrease with increasing the GNPs size and was found to be 2.5, 3.5 and 4 ms for 10, 20 and 50 nm GNP size, respectively.

This study demonstrates that the dielectric, electrical conductivity and relaxation time values decreased with increasing the GNPs size, e.g. these changes are particle-size dependent.

This study suggests that the increase in dielectric constant, electrical conductivity and relaxation time observed with the smaller 10 and 20 nm GNPs as compared

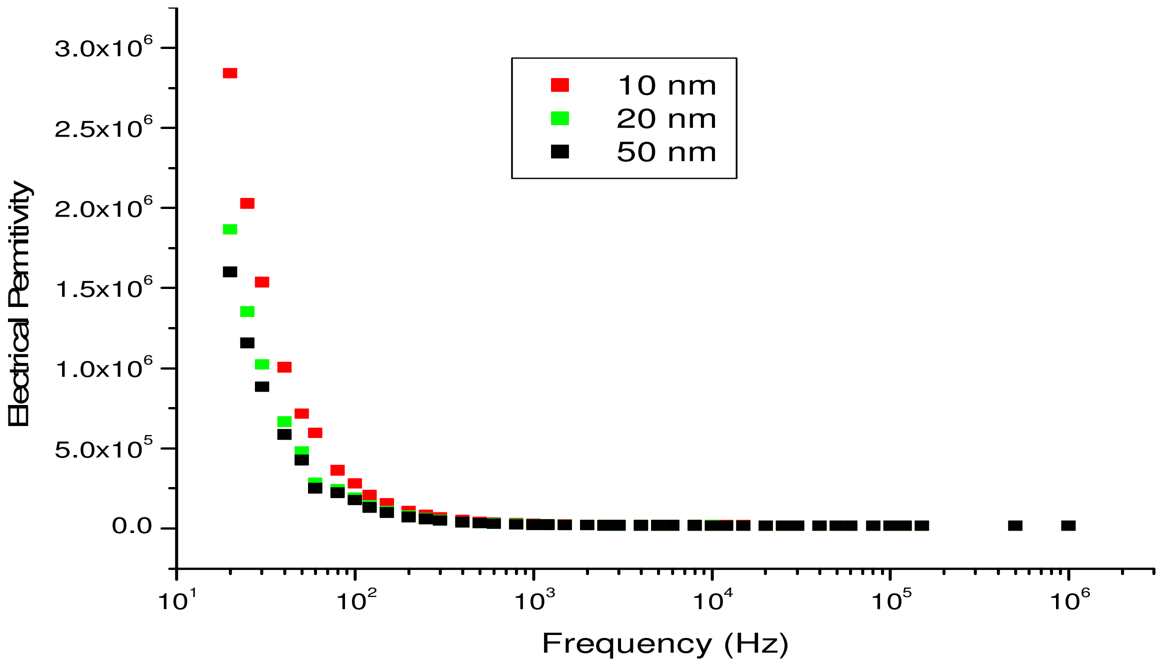

Figure 2. Relative permittivity ε' as a function of the applied frequency in the frequency range of 20 Hz to 1 MHz for 10, 20 and 50 nm GNPs.

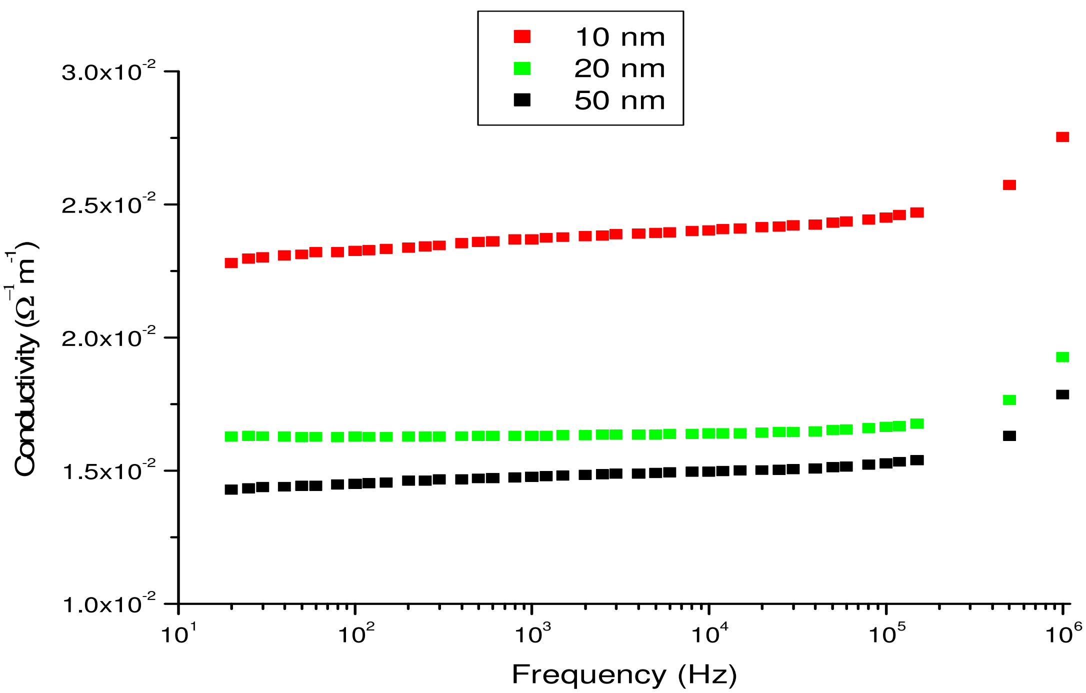

Figure 3. Electrical conductivity (σ) as a function of the applied frequency in the frequency range of 20 Hz to 1 MHz for 10, 20 and 50 nm GNPs.

to 50 nm GNPs may be used as important risk factors for bioaccumulation and toxicity of the smaller GNPs. Thus, to understand and confirm this hypothesis, additional histological and histochemical experiments are needed to investigate the toxicity and bioaccumulation of the smaller GNPs in several tissues.

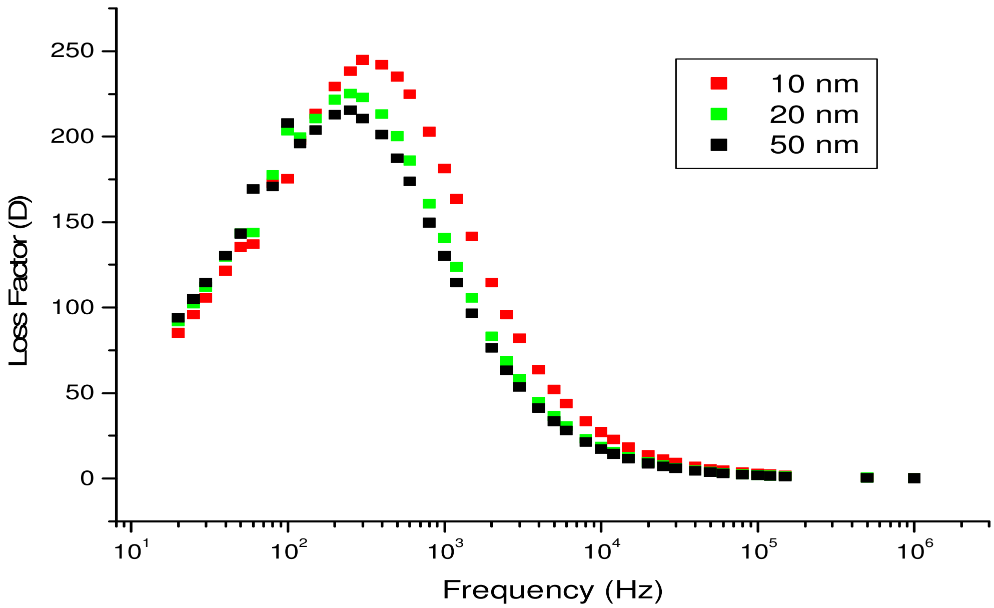

Figure 4. The variation of loss factor (tan δ) with the applied frequency in the range of 20 Hz to 1 MHz for 10, 20 and 50 nm GNPs.

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