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Physical Properties of Different Gold Nanoparticles: Ultraviolet-Visible and Fluorescence Measurements

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Abstract

Background: The light absorption and emission characteristics of Gold Nanoparticles (GNPs) are exploited in detection and treatment of cancer. The properties of Nanoparticles (NPs) give them high potential for use in various medical applications, particularly in diagnostics and therapy where they promise increased sensitivity, speed, and cost-effectiveness. The Ultraviolet-Visible and fluorescence properties of non-functionalized GNPs have not thus far been comprehensively documented. This study evaluated the absorption and fluorescence spectra for solutions of GNPs at different concentrations.

Methods: The mean sizes of these GNPs were calculated from Transmission Electron Microscope (TEM) images, which were also used to study the morphology of the GNPs. UV–Visible and fluorescence measurements, were made from 250-700 nm using 1 cm quartz cuvettes.

Results: When the GNP size changed from 10 nm to 50 nm, the maximum extinction of the Surface Plasmon Band (SPB) shifted from 517 nm to 532 nm in the visible region which may be attributed to the surface plasmon oscillation of free electrons. At constant GNP size, the absorbance was found to be proportional to the concentration of gold. This is because an increased number of GNPs also increases the total surface for surface plasmon resonance. The Photoluminescence (PL) band centre appears at 423 nm. An increase in fluorescence intensity with increase in GNP size was observed. At a fixed GNP size of 10 nm, and with increasing GNP concentration, the intensity of the emission band increased, which was consistent with the changes observed for the surface plasmon band of GNPs.

Conclusions: The absorption intensity and maxima are particle size dependent. The surface plasmon resonance of the gold particles is red shifted (from 517 to 532 nm) with increasing particle size. These results indicate that the fluorescence intensity and the absorption band of GNPs were concentration and particle size dependent.

Keywords: Gold nanoparticles; particle size; absorbance; fluorescence; spectroscopy

Introduction

One particularly exciting field of research involves the use of GNPs in the detection and treatment of cancer cells [1]. Current methods of cancer diagnosis and treatment are costly and can be very harmful to the body. GNPs, however, offer an inexpensive route to targeting only cancerous cells, leaving healthy cells untouched [2].

The very small size of nanoparticles (<100 nm) imparts a large surface to volume ratio, and thus physical and chemical properties are very different from those of the same material in the bulk form. These properties include enhanced or hindered particle aggregation depending on the type of surface modification, enhanced photoemission, high electrical and heat conductivity, and improved surface catalytic activity [3-7].

GNPs have unique optical properties in the visible region, because of surface plasmon oscillation of free electrons [8]. In the bioscience and medical fields, GNPs are used as immunostaining marker particles for electron microscopy, and as chromophores for immunoreactions and nucleic acid hybridization [9-14].

The strong absorption of GNPs can also be used in colorimetric detection of analytes by measuring changes in the refractive index of the environment of the GNPs caused by adsorption of target analytes [15]. GNPs can be used to label DNA or proteins for detection of biological targets with enhanced sensitivity. They are primarily utilized in imaging, and molecular diagnostic applications [16-19]. Finally, GNPs can be used to develop sensitive electrochemical detection methods which can be coupled to enzymatic assays.

The origin of the unique optical properties of GNPs is a phenomenon known as Surface Plasmon Resonance (SPR). The GNP has to be much smaller than the wavelength of the incidence wavelength, as referred to as the quasi-static approximation. These oscillations are known as SPR; they occur within visible frequencies and result in strong optical absorbance and scattering properties of GNPs [20].

UV–visible absorption spectroscopy is the most widely used method for characterizing the optical properties and electronic structure of nanoparticles, as the absorption bands are related to the diameter and aspect ratio of metal nanoparticles. Solutions of colloidal GNPs have a distinctive red colour, which arises from the tiny dimensions of the GNPs. At nanometre dimensions, the electron cloud can oscillate on the particle surface and absorb electromagnetic radiation at a particular energy. GNPs were prepared by both chemical and biosynthetic methods, and the changes in the UV–visible spectra of the resultant colloids were measured to study the size effect of metal nanoparticles on the surface plasmon resonance. Whilst the strong

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surface Plasmon band of GNPs has been widely investigated, studies on the photoluminescence from GNPs are scarce [21].

The properties of NPs give them high potential for use in various medical applications, particularly in diagnostics and therapy. In this study we would like to shed the light on the physical properties of GNPs because these effects have not been documented before. The Ultraviolet-Visible and fluorescence properties of non-functionalized GNPs have not thus far been comprehensively documented. Here we focus our attention in the absorption and fluorescence spectra of GNP solutions as a function of particle size and concentration. We also use Transmission Electron Microscopy (TEM) to evaluate the morphology and exact size of the GNPs.

Materials and Methods

GNP size determination

GNPs with nominal sizes of 10, 20 and 50 nm were purchased (Products MKN-Au-010; MKN-Au-020; MKN-Au-050, MK Impex Corp, Canada) and used in this study. The GNPs were dissolved in aqueous solution to give a concentration 0.01%. The mean sizes, morphology and good particle size distribution for these GNPs were evaluated from the TEM images. The images indicate that the particles are homogeneous in both shape and size. The high electron densities of the GNPs make TEM as an effective way of characterizing their morphology and size.

UV-Visible and fluorescence spectroscopy

UV–visible characterization of solutions of 10, 20 and 50 nm GNPs at concentrations from 0.2×10^{-3}–1×10^{-2}% was performed using a UV-Visible spectrophotometer (UV-1601 PC, Shimadzu, Japan; H14 grating (UV through shortwave NIR with optical resolution of 0.4 nm)). The absorbance measurements were made over the wavelength range of 250-700 nm using 1 cm path length quartz cuvettes, which were cleaned before each use by sonicating them for 5 min in deionized water and then rinsing with deionized water. The pH values of all solutions remained at 6.3.

Fluorescence characterization of the GNP solutions was performed using a FluoroMax-2 JOBAN YVON-SPEX, Instruments S.A., Inc., France. The fluorescence measurements were also made over the wavelength range of 250-700 nm.

Results and Discussion

Size and morphology of gold nanoparticles

The 10 and 20 nm GNPs show spherical morphology while the 50 nm GNPs show hexagonal morphology. All GNPs show narrow particle size distribution and good dispersion in the solution. The mean sizes for these GNPs were calculated from the TEM images. Mean size for 10 nm GNPs was 9.45 ± 1.33 nm, 20 nm GNPs was 20.18 ± 1.80 nm and 50 nm GNPs was 50.73 ± 3.58 nm (Figure 1).

UV-Visible spectroscopy

Figure 2 shows the UV–Visible absorption spectra of 10, 20 and 50 nm GNPs; the maximum in the Au absorbance intensity varies around 517 nm.

The optical properties such as absorption maxima and absorption intensity are particle size dependent. An intense absorption peak at 517 nm is generally attributed to the surface plasmon excitation of small spherical gold particles.

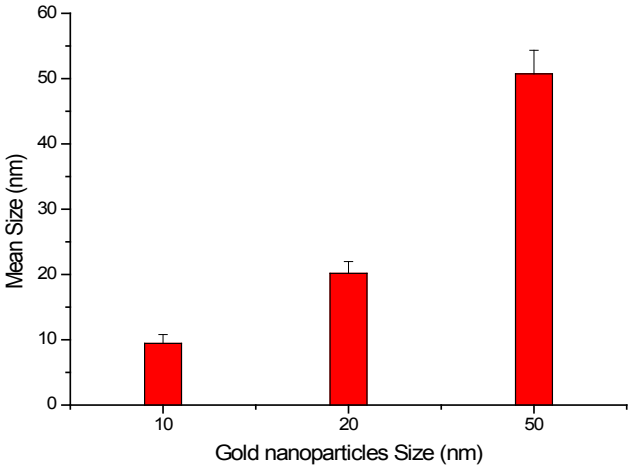

Figure1: The size of different gold nanoparticles (n = 7).

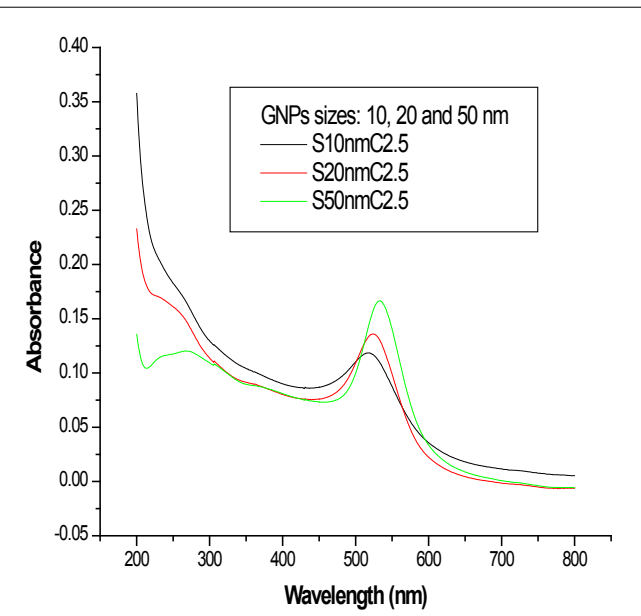

Figure2: The UV–Visible absorption spectra of 10, 20 and 50 nm GNPs.

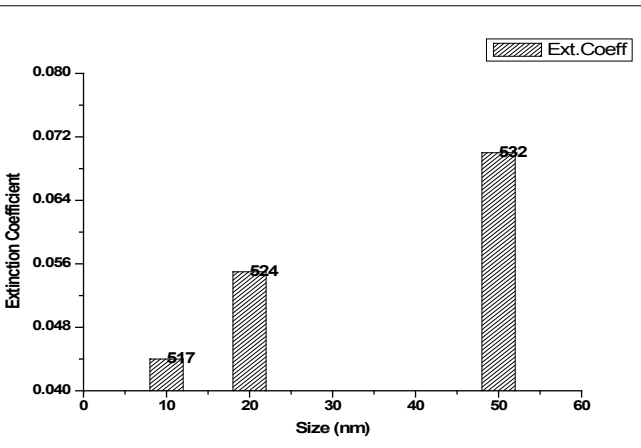

Figure3: The variation in the extinction coefficient with GNPs size.

Figure 3 shows the variation in the extinction coefficient with GNPs size. When the GNP size changed from 10 nm to 50 nm, the maximum extinction of Surface Plasmon Band (SPB) shifted from 517 nm to 532 nm in the visible region which may be attributed to the surface plasmon oscillation of free electrons. The surface plasmon resonance of the gold particles is red shifted with increase in particle size in accordance with Mie theory [22].

Figure 4 shows the variation in the absorbance of 10, 20 and 50 nm GNPs with concentration (0.2×10^{-3}–1×10^{-2}%). At a constant GNP size, the absorbance was found to be proportional to the concentration of gold. This is not surprising, since the increased number of nanoparticles also provides increased surface for surface plasmon resonance.

The optical properties of gold are due to 5d (valence) and 6sp (conduction) electrons. The outermost d and s electrons of the constituent atoms must be treated together leading to six bands: five of them are fairly flat, lying a few eV below the Fermi level, and are usually denoted as d bands; the sixth one, which is almost free-electron like is known as the conduction band or sp band [23].

Single photon luminescence from gold has been described [23,24] as a three-step process as follows: (i) excitation of electrons from the occupied d to the sp band which is above the Fermi level to generate electron–hole pairs, (ii) scattering of electrons and holes on the picosecond time scale with partial energy transfer to the phonon lattice and (iii) recombination of an electron from an occupied sp band with the hole resulting in photon emission.

Fluorescence spectroscopy

The fluorescence spectra of 10, 20 and 50 nm GNP solutions measured with an excitation wavelength of 308 nm are displayed in Figure 5. The centre of the photoluminescence (PL) band appears at 423 nm. An increase in fluorescence intensity with increasing GNP size was observed. The incident light at 308 nm will lead to excitation of the surface plasmon coherent electronic motion as well as the d electrons. The applied concentration for each particle size was included in Table 1.

At a fixed GNP size of 10 nm, the intensity of the emission band increased with increasing GNP concentration, and the trend was consistent with the changes corresponding to surface plasmon band of GNPs (Figure 6). These results indicate that the fluorescence emission band intensity and the absorption band of GNPs were concentration and particle size dependent.

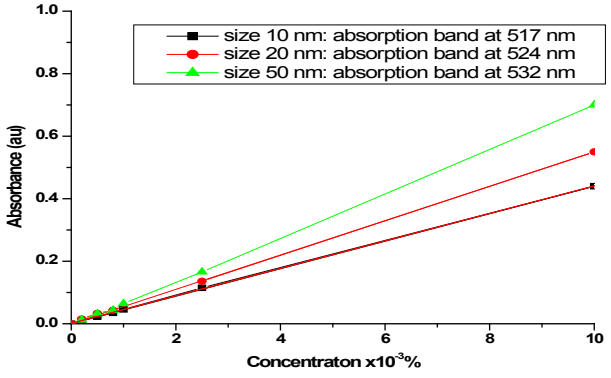

Figure4: The variation in the absorbance of 10, 20 and 50 nm GNPs with concentration.

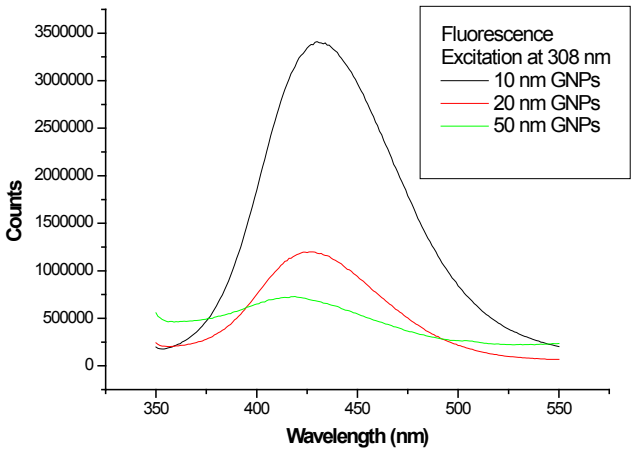

Figure5: The fluorescence spectra of GNP solutions measured with an excitation wavelength of 308 nm.

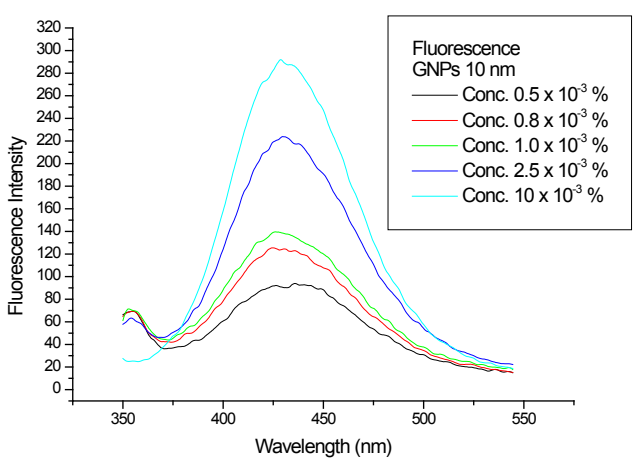

Figure6: The emission fluorescence peak intensity for GNP of size 10nm at different concentrations.

When quantitative analysis was performed on the fluorescence spectra, the fluorescent intensity was increased linearly as the concentration goes higher with correlation coefficient R2 = 0.995.

The results of this study are of high significance to the field of nanotechnology for these reasons: Advances in nanotechnology have identified promising candidates for many biological and biomedical applications. Since the properties of NPs differ from that of their bulk materials, they are being increasingly exploited for medical applications. Nanoparticles (NPs) have potentially caused adverse effects on organ, tissue, cellular, subcellular and protein levels due to their unusual physicochemical properties [25-30].

Abdelhalim and Jarrar [26-29], 2011 and 2012 have reported that intraperitoneal administration of different sizes of GNPs induced toxicity in several organs such as liver, heart, kidneys and lungs that became unable to deal with the accumulated residues resulting from metabolic and structural disturbances caused by these NPs. These alterations were size-dependent with smaller ones (10 nm GNPs) induced the most effects and related to time exposure of GNPs [25-30].

The appearance of hepatocytes cytoplasmic degeneration and

Product type	Product # MKN-Au-010 Gold nanoparticles in aqueous solution	Product # MKN-Au-020 Gold nanoparticles in aqueous solution	Product # MKN-Au-050 Gold nanoparticles in aqueous solution
Number of particles/mL	5.7 x 10^{12} particles/mL	7.0 x 10^{11} particles/mL	4.5 x 10^{10}particles/mL
Concentration	Concentration: 0.01% Au	Concentration: 0.01% Au	Concentration: 0.01% Au
Size	Size: 10 nm	Size: 20 nm	Size: 50 nm

Table1: The applied concentration for each particle size.

nuclear destruction may suggest that GNPs interact with proteins and enzymes of the hepatic tissue interfering with the antioxidant defence mechanism and leading to Reactive Oxygen Species (ROS) generation which in turn may induce stress in the hepatocytes to undergo atrophy and necrosis. One possible way of avoiding significant toxicity is to coat the GNPs with biocompatible polymers. Now-a-days other experiments to effectively demonstrate and avoid the possible side effects of GNPs in the *in vivo* studies are taken in consideration and conducted [26,29].

Conclusions

The aim of the present study was to investigate the absorption and fluorescence spectra for 10, 20 and 50 nm GNPs at concentrations from 0.2×10^{-3} to 1×10^{-2} %.

The high electron density and homogeneity of GNPs make them highly conspicuous under the TEM.

The maximum absorption of SPB shifted from 517 nm to 532 nm, when the GNPs size changed from 10 nm to 50 nm which might be attributed to the surface plasmon oscillation of the free electrons. At a constant GNP size, the absorbance was proportional to the concentration of gold. The fluorescence emission band of the GNPs varied with GNP size and concentration. The fluorescence emission band intensity increased with increasing GNP size and concentration.

This study demonstrates that the absorption and fluorescence spectra for different GNP sizes were size and concentration-dependent.

Further experiments using absorbance and fluorescence spectra are required to be performed after the administration of GNPs through different routes in rats *in vivo*.

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