Behavioral Understanding of Silver Nanoparticles using Maxwell's Equations

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Abstract: **In recent years, innumerable applications of silver and gold nanoparticles in the field of medicine, agriculture, industries, especially in textile and garment industries due eco-friendly behaviour and health awareness, for this purpose a burst of research activities has been seen in the synthesis and characterization of noble metals like Nano gold and Nano silver particles in the field of physics and chemistry, but calculations like absorption, extinction and scattering coefficients using mathematical simulations by Mie's theory playing important role in the field of basic sciences, since materials in the nanometer regime display wonderful size-dependent optical, electronic, magnetic, chemical and medicinal properties, which are remarkably different from its bulk behavior. There are numerous possible applications for such Nano scale materials in developing industrial and medical fields especially textile and fabric industries, due to its unique property of high surface area and exceptional surface activity. These nanoparticles with different sizes show the different extinction, absorption and scattering coefficients. These coefficients can be easily evaluated with the help of mathematical Maxwell"s Electromagnetic and Mie's scattering theory. These size calculated Nanoparticles are very important in the fabric design technology in the textile industries.**

***Keywords*: Extinction, Absorption, Scattering, Silver nanoparticles.**

I. INTRODUCTION

Nanoscience and nanotechnology are recent revolutionary developments of science and technology that are evolving at a very fast pace since a decade. They are driven by the desire to fabricate materials with novel and improved properties that are likely to impact virtually in all areas of physics, chemistry, biology, medicine and other interdisciplinary fields of science and technology. Particles with sizes in the range of 1-100nm are called nanoparticles, whether they are dispersed in gaseous, liquid or solid media. Nanoparticles are a number of atoms or molecules bonded together (about 10^6 atoms) and are intermediate in size between individual atoms and aggregates large enough to be called bulk material. Because the nanoparticles are larger than individual atoms and molecules but are smaller than the bulk solid, materials in the nanometer size regime show behaviour that is intermediate between macroscopic solid and that of an atomic or molecular system. There are three major factors [1-5] that are responsible for these differences:

1. High surface to volume ratio.
2. Quantum size effect.
3. Electro dynamical interactions.

Metallic nanoparticles possess unique optical, electronic, chemical and magnetic properties that are strikingly different from those of the individual atoms as well as their bulk counterparts. Nano (10^{-9}m) sized metal particles exhibit optical properties of great aesthetic, technological and intellectual value. Colloidal solutions of the noble metals namely, silver and gold show characteristic colours that have received considerable attention to researchers.

Metal nanoparticles, especially gold and silver; have attracted considerable attention recently because of their many interesting properties [6] and innumerable technological and medical applications. The optical properties of isolated gold and silver nanoparticles have been extensively studied. Bulk gold has a familiar yellow colour, and silver has peculiar silver colour, caused by a reduction in reflectivity for light at the end of the spectrum. Whenever gold or silver is sub divided into smaller and smaller particles, the ratio of the radius to the wavelength becomes important, and when the particle is smaller than the wavelength, the Rayleigh approximation (i.e., no retardation) holds and the mathematics becomes simple. Mie [7] has shown that Plasmon excitation is present when the radius is large compared with the wavelength of light, and in that case, the retardation effect should be included to get the correct results. When the particles of gold are small enough, their colour is ruby red, due to their strong absorption of green light at about 545nm, corresponding to the frequency at which a Plasmon resonance occurs with the gold [8]. When the dimensions of the conductor are reduced, boundary and surface effects become very important, and for this reason, the optical properties [9] of small metal nanoparticles are dominated by collective oscillation of conduction electrons. An absorption band results when the incident photon frequency is resonant with the collective oscillation of the conduction band electrons and is known (Fig 1) as the Surface Plasmon Resonance (SPR).

Metal nanoparticles are of great current interest due to their functions as chemical catalysts, adsorbents, biological stains, and elements of novel nanometre scale optical, electronic, and magnetic devices, as the size of the particle decreases to 1-100nm range, it is well-known that the electronic, optical, catalytic and thermodynamic properties of metal particles deviate from bulk properties. Mie presented a solution to Maxwell's equations [10-12] that describes the extinction spectra (Extinction efficiency = scattering efficiency + absorption efficiency) of spherical particles of various size. Mathematical Mie's solution remains of great interest to this day, but the modern generation of metal nanoparticle science, including applications to medical diagnostics and Nano optics has provided new challenges for theory. In this paper, we highlight recent advances in theoretical research in this area, emphasizing especially the linear optical properties (extinction, absorption, scattering) of isolated silver nanoparticles of various shapes in nanometre regime. These highly size tuned nanoparticles are playing vital role in the designing of fashion based fabrics in textile industries. Now the time has been up to meet the textile industries to meet the antibacterial cloths to meet the various pandemic diseases. During the pandemic situation peoples are severely suffering due to bacterial and viral problems can be ruled out due to futuristic Nano-fabric clothes and masks.

Experimental and Simulation:

Optical absorption and fluorescence were recorded using Ocean Optics HR4000 high resolution spectrometer instrument it includes monochromator ultraviolet and visible source which provides 200 to 700 nm light. Computational electrodynamics calculations like absorption, scattering and extinction efficiencies are calculated using nanohub.org simulations which is available online. Graphical representations are done through Origin 6.1 software.

Synthesis and analysis of silver nanoparticles was done using computational electrodynamic calculations and are available in the nanohub.org simulation software. The tool we will be used in the present study is "Nanospehere Optics Lab", and is based on the Mie's theory.

Theoretical Studies:

Optical properties of isolated colloidal particles in particular, their dependence on particle size have been intensively investigated through mathematical Mie's scattering theory. In particular Mie's theory [10, 19-20] is a mathematical and physical description of the scattering of electromagnetic radiation by spherical particles immersed in a continuous medium. The Mie scattering solution begins with Maxwell's equations. Using the complex representation of electric field E and the magnetic field H, the Maxwell's equations are of the form,

$$\nabla \cdot E = 0 \quad 3.1$$

$$\nabla \cdot H = 0 \quad 3.2$$

$$\nabla \times E = i\omega\mu H \quad 3.3$$

$$\nabla \times H = -i\omega\varepsilon E \quad 3.4$$

The configuration of an incident electromagnetic field with two components, the electric field E and the magnetic field H can be described by the Helmholtz's relation [19-20] as

$$\nabla^2 E + k^2 E = 0 \quad 3.5$$

$$\nabla^2 H + k^2 H = 0 \quad 3.6$$

In which k is the wave number defined by

$$k^2 = \omega^2 \varepsilon\mu \quad 3.7$$

The effect of the particular size on the peak resonant wave length results from two different mechanisms depending on the particle size range. In the limit of 2R<< λ (where R is the radius of the particles and λ is the wave length of the light in media), only the electric dipole term contributes significantly [1,7,10,21] to the extinction cross section (σ_{ext}) is,

$$\sigma_{ext} = 9\frac{\omega}{c}\varepsilon_m^{3/2} V \frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega)+2\varepsilon_m]^2 + [\varepsilon_2(\omega)]^2} \quad 3.8$$

Where $V = \left(\frac{4\pi}{3}\right) R^3$ is volume of the spherical particle.

$$\sigma_{abs} = \sigma_{ext} - \sigma_{sca} \quad 3.9$$

ω is the angular frequency of the exciting light, c is the velocity of light, ε_m and $\varepsilon(\omega)$ [$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$] are the dielectric frictions of the surrounding medium and the material itself respectively. The resonance condition is fulfilled when $\varepsilon_1(\omega) = -2\ \varepsilon_m$ provided ε_2 is small or weakly dependent on ω.

The ability to assemble nanoparticles of controllable sizes and shapes is increasingly important because many frontier areas of research, such as sensors, catalysis, medical diagnostics, information storage, and quantum computation, require the precise control of nanomaterial architecture and component miniaturization. In nanotechnology, the assembly of metal nanoparticles has resulted in novel materials with interesting properties, i.e., extremely high extinction coefficients and the strongly distance-dependent.

II. RESULTS AND DISCUSSION

In the present case the absorption spectrum of AuNP's has a maximum in the range 480-490nm peaking at 485nm, which is related to the Plasmon resonance formed due to the Nano sized (4-12nm) silver particles. This absorption band results from interactions of free electrons confined to small metallic spherical objects with incident electromagnetic radiation. The observed Plasmon resonance band (Fig 1) shows that the silver nanoparticles are spherical in shape.

Extinction coefficient is sum of absorption and scattering coefficients (Table 1). Scattering arises when charged particles accelerated by a field and reradiate. Absorption (Fig 2) occurs when the particle takes energy out of the beam and converts it to other forms. Mie's expression for Extinction efficiency is given by Eqn 3.8, the extinction efficiency spectrum for several nanoparticle radii can be seen in (Fig 3). The wavelength corresponding to maximum extinction shifts to longer wavelengths (red shift) as the particle radius increases. The peak seen at 485nm corresponds to the resonance condition for small spheres specifically when $\varepsilon_1(\omega)= -2\ \varepsilon_{m.}$ A large shift of the dipole peak and a much more complex spectrum occur when the particle radius is increased further.

Since the dielectric medium constant (ε) is related to refractive index, [9-11, 22] i.e., $(n_{eff} + ik_{eff})^2 = \varepsilon_{eff}$ (ε_{eff} is the effective dielectric constant of the nanocomposite, n_{eff} is the real part of the effective complex index of refraction for the nanocomposite, k_{eff} is the imaginary part of the effective complex index of refraction), we show here that the evolution of the SPR band at the longer wavelength region can be considered a result of the increase in effective refractive index for nanoparticles in the assembly, in the assembly process, the size of individual silver nanoparticles in the solution should remain largely constant, whereas the inter particle distance changes, which leads to changes in the inter particle dielectric medium constant or refractive index. Refractive index n will be used to represent the n_{eff}. Interestingly, the change in n was found to exhibit an approximate linear relationship with λ_{max}. Simulation results for silver nanoparticles for various sizes 10-55nm particles using Mie's theory, which matches with the bands in terms of the SPR wavelength as observed. On the basis of the documented principle that the Plasmon red shift increases with refractive index change, a basic assumption for applying the Mie's theory simulation to this system is that the nanoparticles within the assembly environment have a refractive index higher than that in the water environment. This assumption is qualitatively supported by the trend of refractive index changes reported in previous studies for similar assemblies of metal nanoparticles in different systems. The effect of electromagnetic retardation in larger sized nanoparticles makes the observed red shift in the Plasmon resonance.

Fig 2 to 6 shows the calculated spectra of the efficiency of absorption, scattering and extinction for silver nanoparticles of radius 10-55nm in size. The dimensionless efficiencies can be converted to the corresponding cross-sections $\square_{abs}$, $\square_{ext}$ and $\square_{sca}$ have units of m^2 because they represent an equivalent cross-sectional area of the particle that contributes to the absorption, scattering and extinction of the incident light.

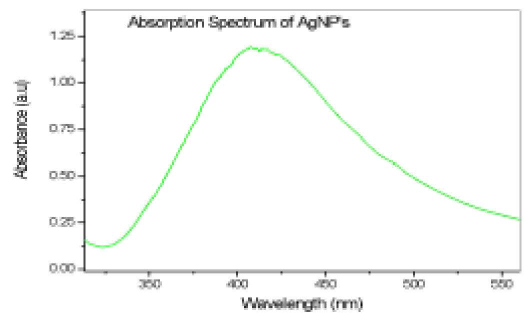

Figure 1. Plasmon resonance absorption spectrum of AgNP's in aqueous solution.

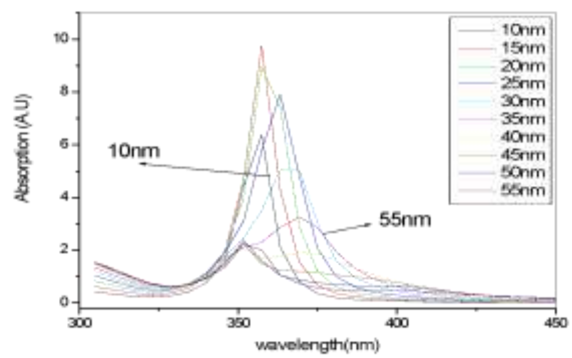

Figure 2. Absorption coefficient of silver nanoparticles of various sizes from 10-55nm.

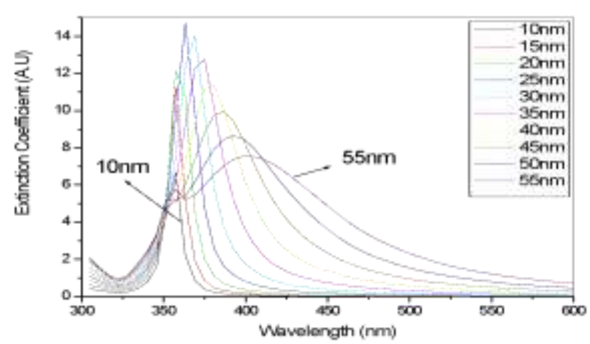

Figure 3 Extinction cross section of silver nanoparticles of various sizes from 10-55nm.

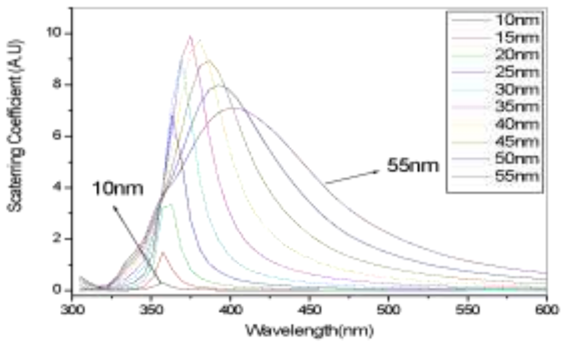

Figure 4. Scattering cross section of silver nanoparticles of various sizes from 10-55nm.

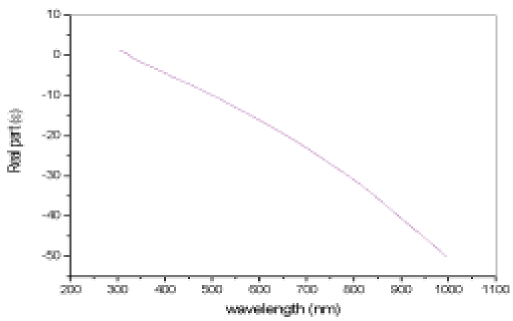

Figure 5. Real part of dielectric constant of silver nanoparticles.

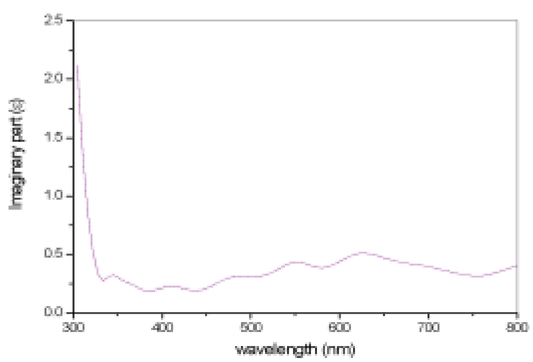

Figure 6. Imaginary part of dielectric constant of silver nanoparticles.

III. APPLICATIONS OF NANOPARTICLES IN TEXTILE INDUSTRIES

In Recent days, there is mounting interest of the use of silver based nanomaterials as antimicrobial mediators in the textile sector as well. Germ-free fabrics are one of the collective goal defined by the scientists so there would be the bacterial free fabrics subject to the various different conditions. The dissimilar usage of nanomaterials for textile fabrics has been continuously demanded due to increasing customer costumes for different purposes. To functionalize fabrics, the nano-moieties can play the major role with their specific properties. The various properties of fabrics such as stimulate stain repellent, wrinkle free, antistatic, strength enhancement; water repellent and antimicrobial are very significant to enhance fabric durability, luxuries and flexibility. Textile industries have changing and adopting new technologies not only in fabric processing but also in the use of antimicrobial agent to avoid bacterial contamination. Currently, peoples are also aware about bacterial infections occurred due to textile products. The spreading of microorganisms from fabric surfaces to the human skin is the major health concern. Therefore, fabrics can be treated to avoid bacterial infections [23]. In current scenario, textile fabrics have different properties such as antimicrobial activity, UV protection and self-cleaning. The contemporary methods in textiles have adopted nanotechnology in order to accomplish antimicrobial property. But, in this direction selection of proper antimicrobial agent is a challenging task. The choice of Ag NPs is preferable as compared with traditional antimicrobial agents such as metal salts, quaternary ammonium compounds and triclosan. This is superior due to various factors such as bacterial resistance, stability, cheaper and environmental benign. Therefore, it is more useful than the ionic silver as they cannot generate stain on the fabrics, maintaining fabric breathability and handling. The antimicrobial agent in bare or composite form on the fabric cannot leads to the decolourizations or of destruction of mechanical strength of fibre. Cotton fabric exhibits self-cleaning properties under visible light by anchoring its surface with Ag@ZnO nanostructured materials. In addition, the preparation of lightweight and wearable clothes with antimicrobial activity the polyamine-mediated bioinspired approach is simple for functionalization of antimicrobial agents on the surfaces. Nanostructured materials are formed by using polyamines which is coated on the surface of fabrics for better antimicrobial activity under the sunlight. It also exhibited proficient photocatalytic, self-cleaning and stain removal property of the fabric. Plasma pre-treated polyamine coated with Ag NPs are studied for antimicrobial activity and aging effect. The bacterial inhibition is observed after 30 days in the presence of Ag NPs with size <100 nm. Furthermore, a longer period bacterial inhibition is observed at lower concentration with 40–60 nm size Ag NPs. Plasma treated polyester fabric developed for increasing binding property of Ag NPs and pre-treatment initiated both ionic and covalent interactions to create oxygen species on the fibres, resulting deposition of smaller size Ag NPs which promote antimicrobial property. The functional clothing has good scope in the market because it has designed to get better performance to the user in the extreme conditions. The various functional clothing such as protective, medical or sport clothing are available in the market. In functional clothing studies have been focused on antimicrobial effects in laboratory scale to the real life conditions. Now a day's engineered nanoparticles (ENPs) are the new technology, in which functionalized silver and titania based consumer products are used as antimicrobial and photoactive agents. However, the various external exposure pathways such as the contact between fabric and skin as well as ingestion and inhalation transfer to children by oral routes are responsible for toxicity to human cell lines. These ENPs uptake rates on skin have less exposure therefore they are exhibited less toxicity than oral pathways used in dietary supplements. Silver coating by various techniques on the textile fibres having longer period of release of silver ion and uniform distribution of silver on fabric is important parameter for antimicrobial fabrics. In the realistic approach leaching of silver from fabrics used for children is studied in the presence of different liquids such as water, milk, sweat and urine. Subsequently, leaching of silver in presence of sweat and urine found to be higher than the tap water. This study reveals the less connectivity of silver particles to the fabrics; which would be further optimized for decreasing the leaching rate of Ag NPs from the fabrics so that these particles would not be harmful to the human beings. Fig 7 shows the antimicrobial efficacy of Ag NPs in the textiles. Microbial efficacy of Ag NPs was determined on the textile fibres during various life cycle stages. Multiple cycles washing exhibited range of silver release but does not affect antimicrobial efficacy of Ag NPs.

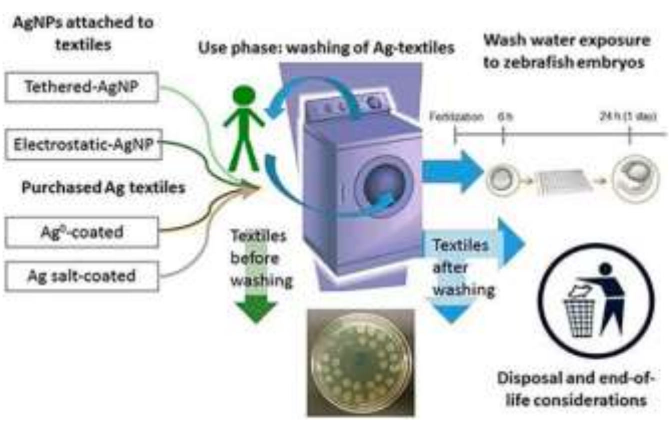

Fig 6. Antibacterial character of Nanoparticle fabricated clothes washing

IV. CONCLUSION

The optical properties of spherical silver nanoparticles can be tuned by adjusting the physical dimensions. The dielectric properties of the material are extremely important and play a large role in the intensity and placement of the Plasmon resonances. As spherical nanoparticles get larger, the peaks broaden and shift to longer (red shift) wavelengths. This shift of the SPR of the band position and intensity of the nanoparticle assembly can be related to the change in dielectric medium of RI properties, which provides a means to produce optical signals for up taking or releasing of molecular species in the nanoparticle assembly. This type of inter particle property also has potential applications in controlled drug delivery (1-5), in regard to the exploitation of these Nano materials for application in electrical sensors, the electrical response of nanoparticle assemblies to vapour sorption serve as an excellent example illustrating the correlation of the electrical properties with inter particle dielectric medium properties, The understanding of the precise control of the inter particle properties will benefit these nanostructured sensing applications. These mathematical simulations carried out during the present work is useful to tuneable the properties of central development in Nano science and nanotechnology. In view of this we have highlighted some recent progress towards the development of basic physics and chemistry in the field of Nano science and nanotechnology which opens up the new avenues towards latest advances in the field of mathematics and physics.

Table 1. Observed Extinction, Absorption and Scattering efficiencies of silver nanoparticles of various sizes in the surrounding water medium.

Radius of the nanoparticle (nm)	**Position of λ_{max} (nm)**	**Extinction efficiency**	**Absorption efficiency**	**Scattering efficiency**
10	357.53	6.673	6.380	0.293
15	357.33	11.256	9.757	1.499
20	357.53	12.172	8.953	3.323
25	363.38	14.739	7.923	6.816
30	369.23	14.039	5.032	9.007
35	375.08	12.757	2.860	9.897
40	380.93	11.358	1.613	9.745
45	386.78	9.941	0.983	8.958
50	392.63	8.637	0.654	7.983
55	404.33	7.545	0.448	7.096

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