RSC Advances




ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

# Observation of Weak Localization of Light in Gold Nanofluids Synthesized using Marine Derived Fungus *Aspergillus niger*

Vishakha Dave[1], Anjana K. Vala[2], Rajesh Patel[1,]*

[1]Department of Physics, Maharaja Krishnakumarsinhji Bhavnagar University, Bhavnagar. 364002. India.

[2]Department of Lifesciences, Maharaja Krishnakumarsinhji Bhavnagar University, Bhavnagar. 364002. India.

*Corresponding Author: rjp@mkbhavuni.edu.in ; rpat7@yahoo.com

## Abstract

We have observed weak localization of light for the first time in gold nanofluids synthesized using marine derived fungus *Aspergillus niger*. Coherent backscattering of waves by a disordered scattering medium is responsible for weak localization of light. We have directly observed this effect using polarized visible light and for different sizes of gold nanoparticles in nanofluids. The localization parameter $kl^*$ obtained from the observation is $1<kl^*<5$, which is the precondition for the weak localization of light. The $kl^*$ is controlled by the size and concentration of the particles in the nanofluids. Quadratic scaling is used to study the localization transition. The localization length obtained is nearly 225 nm. Gold nanoparticles have potential applications in biomedicine, imaging, catalysis and photonics.

Key word: localization of light, gold nanofluid, biosynthesization

## Introduction

Invisibly small particles of gold can be used to manipulate the properties of light[1]. There has been a growing demand of gold nanoparticles due to its application potentiality to improve efficiency of polymer solar cell [2], to produce plasmonic grating [3], in diverse applications in the field of biomedicine, catalysis, imaging, photonics, localized surface plasmon resonance, etc. [4-10]. Enhanced optical trapping and sensitivity coupled with significant heating is studied using gold nanoparticles [11].

Propagation of light waves in disordered, strongly scattering dielectrics is complex and full of surprises [12]. Complex dielectric are structures in which the dielectric constant varies on length scales that are roughly comparable to the wavelength of light. In disordered dielectric structures light wave undergo a complicated multiple scattering process. Interference effect can survive random multiple light scattering and lead to interesting phenomena like speckle correlations, universal conductance fluctuations of light, and optical Anderson localization [12,13]. The most robust of the interference phenomena is weak localization of light [14-20], which originates from the fundamental concept of reciprocity and is observable as a coherent enhancement of the intensity in the back scattering direction. This enhancement is called the cone of coherent backscattering. Since the first experimental observation of coherent backscattering from colloidal suspension [15,16], the phenomenon has been successfully studied in various random materials like powders [21], photonic crystals [22], cold atom gases [23], and liquid crystals [18]. Very recently, light localization is used to generate the heat in nanoparticles suspension [22].

In this paper we report observation of weak localization of light for the first time in gold nanofluids synthesized using marine derived Fungus *Aspergillus niger*. Bio synthesis of Gold

nanoparticles (GNP) has several advantages over conventional synthesis of GNP, it is cost effective and enviornment friendly, it does not use any toxic chemical in the protocol [25,26]. Experimentally we have measured the enhancement of the intensity in the backscattered direction i.e. the coherent backscattering cone for the two particle size 15nm and 35 nm in aqueous suspension. This observation allowed us to determine the width of the backscattering cone and estimate the transport mean free path. The localization parameter $kl^*$ obtained from the observation is $1<kl^*<5$. To study the localization transition quadratic scaling is used and the transmission is plotted as a function of inverse of sample thickness. Thus the localization length obtained is nearly 225 nm.

**Experimental**

***Isolation, identification of test fungus and biosynthesis of gold nanofluid***

The test fungi were isolated from sea waters of Bhavnagar coast (Latitude $21^0 45'$ N and Longitude $72^0 14'$ E), Gulf of Khambhat, West Coast of India. The isolate was grown and maintained on potato dextrose agar (PDA, Himedia) medium and stored at 4 8C until use. The medium was prepared in aged seawater and distilled water at a ratio of 3:1. One millilitre inoculum (spore suspension 106/ml) was inoculated in 250 ml PDA medium (prepared in 75% 'aged' seawater). The inoculated flasks were incubated at room temperature for 4 days. After incubation period, the fungal biomass was separated from the medium by filtration and washed extensively with sterile distilled water. Identification of the test strain (A101) was carried out by their macroscopic and microscopic characteristics. Confirmed identification was carried out by the Agharkar Research Institute, Pune. Identification of the fungal isolate was carried out using D2 region of the Large SubUnit: 28S rDNA-based molecular technique. Marine-derived fungus *Aspergillus niger* has been observed to biosynthesize GNPs at different Au(III)

concentrations[23,24]. Further, effect of pH on GNP biosynthesis by this fungus was examined. For this, approximately 5g fungal biomass was exposed to 100ml of1mM gold chloride ($HAuCl_4$) in the pH range 7-10. The inoculated flasks were incubated at $27^0$C for 72 h under static condition. Negative and positive controls were also run along with the experimental flasks. The aqueous solution of GNPs biosynthesized at pH 7 (particle size 35nm) and pH 10(particle size 15nm) were subjected to further experiments. Fig.1 shows the typical TEM image for the synthesized gold nanoparticles.

***UV-vis spectrometry***

Uv-visible spectra were obtained using Elico BL-198 Uv-vis spectrophotometer. For this, two ml sample from each flask was withdrawn (at predetermined time interval) and the spectra were recorded in the range of 400-750nm (1 nm resolution). The experiments were carried out in triplicates. This spectrometer is composed of deuterium, quartz halogen light source with silicon photodiode detector, attached to a computer. The statistical parameters of absorbance spectra were determined approximating data with Gaussian distribution.

***Backscattering experiment***

The typical experimental setup used is schematically depicted in Fig 2. The set up was similar to that described in ref. [14]. A 10mW He–Ne polarized laser at 632.8 nm was collimated to diffraction limit. The collimation was checked by shear interferometry. Following the standard practice, the CBS light was viewed through a non-polarizing 50–50 beam-splitter (anti-reflection coated) with a small wedge. A detector with translating stage was placed to analyze the angular peak. The laser beam was linearly polarized. The free beam going through the beam-splitter was carefully damped. The set up was aligned by placing a mirror in place of the sample and making the reflected beam go back into the laser. The beam transmitted by the beam splitter was scanned

by the detector at the focal plane and the intensity profile so obtained was used as the resolution curve characterizing the system response. This was well described by a Gaussian having a FWHM of 0.2mrad. The aqueous suspension of the gold nanoparticles were taken in a cuvette of 10mm path length. It was placed slightly tilted to the incident beam so that the specular reflection was well away from the backscattered direction. The Brownian motion of the gold nanoparticles in an aqueous suspension caused an ensemble average over the speckle and symmetric peaks were observed.

**Result and Discussion**

Exposure of *Aspergillus niger* biomass to Au(III) solution of different pH (7,8,9,10) resulted in change in color of the solution ranging from pink to ruby red which revealed that the test fungus could synthesize GNPs extracellularly at all test pH. Color of the test solution changed to reddish pink with increasing pH. This is suggestive of decrease in particle size with increase in pH, as shown in Fig.3. Nucleation and formation of number of particles with smaller diameter are facilitated at higher pH. Certain proteins are highly active in alkaline range [27,28], hence, formation of nearly mono-disperse smaller size particles with increase in pH of the test solution could be achieved. Mittal et al., [29] observed aggregation of gold nanoparticles when biosynthesized above and below pH by yeast *Geotrichum candidum*. Irawani and Zolfaghari [27] reported stability and aggregation as one of the issues involved with biosynthesis of metal nanoparticles, the particles biosynthesized in the present study showed noteworthy stability in suspension, even after one year of synthesis, the particles were observed to be very well dispersed. Das et al., [30] suggested electrostatic mechanism as the main stabilization factor for gold bio-nano conjugate.

Physical properties of nanoparticles can be comprehended by analyzing the surface plasmon resonance spectra. Fig.4 shows UV-vis spectra for the biosynthesis of gold nanoparticles by *Aspergillus niger* at different pH. The peak observed is the characteristic peak for the gold nanoparticles at around 540 nm wavelength. Occurrence of a single peak indicates spherical shape of particles. The highest absorbance was observed is in the range of 533.5 nm to 531nm wavelength (for pH 7 to pH 10), as the difference is very small the shift is not clearly visible in Fig 4. As Fig.4 reveals biosynthesized GNPs in the present study are all spherical in shape. According to Mie's theory [29] colloidal particle shape determines the number of SPR peaks. A single peak corresponds to spherical particles while two or more peaks suggest disc or triangular shape of particles, respectively.

Coherent backscattering (CBS) of light occurs in all disordered media and is the only major surviving interference effect. When a beam of light is incident on a random medium, there exist partial waves traversing every possible path in the medium. The CBS effect arises from the constructive interference of any partial wave with its time reversed counterpart in the medium. In exactly the backscattered direction, both these two waves have the same phase and constructive interference results. Away from the backscattered direction, the counter propagating paths develop a phase difference depending on the relative positions of the first and last scattering events in the medium. For the ensemble of all possible light paths, these phases will randomize and the reflection is enhanced within a narrow cone in the backward direction with an angular width of the order of $\lambda/l^*$ where $\lambda$ is the wavelength of light and $l^*$ is the transport length in the medium. This peak shows up only after the ensemble averaging over the large scale sample specific fluctuations (speckle) that originate from the random medium. The set of relevant transport parameters are the mean scattering length $l=1/\langle\rho\sigma\rangle$, defined as the reciprocal of the

average of the product of the single particle scattering cross-section (σ) and the density of the scatterers (ρ), the anisotropy factor <cosθ> which is defined as the average of the cosine of the scattering angle for a single scattering event and the mean transport length ($l^*$) which is a measure of a distance in which, the direction of the photon's motion becomes uncorrelated with its initial direction and is related as $l^*=l/(1-\langle\cos\theta\rangle)$.

In Fig.5 the backscattered intensity is plotted as a function of the angle for two different particle size in gold nanoparticle aqueous suspension. The coherent enhancement at backscattering is between 1.8 and 1.6, consistent with the requirement that the enhancement factor should be lower than 2. The observed value is typical for the experiments with linear polarized light, in the colloidal suspension the ensemble average is conveniently obtained by the Brownian motion of the colloidal particles suspended in the carrier [15,16,21,32]. Fig.5 confirms that the experimental data correspond well to the classical theoretical cone shape. The angular width of the backscattering cone (measured at full width at half maximum) is directly related as $w = 0.7(kl^*)^{-1}$ for the Gaussian disorder as shown in Fig.5. The width w is obtained from the Fig.5 and thus calculated the scattering mean free path l, transport mean free path l*, and the localization parameter kl* listed in Table-1. The width w is inversely proportional to the mean path observed which is in agreement with the theoretical descriptions $w\propto\lambda/l^*$. It is also observed that as the size of the scatterer increases the kl* decreases whereas the width w increases. In these calculations the <cosθ> obtained is 0.93. The results obtained are in agreement with the experimental numbers listed in ref. [13,14,19,30]. To observe a possible localization transition, we have measured the transmission coefficient as a function of inverse of sample thickness (L) for the nanofluid containing 35nm gold nanoparticles. Fig. 6 shows the experimental results for the particle size 35 nm of gold particles. The dashed line is the theoretical curve for the classical

diffusion with $l$ = 11.27 nm. The solid line is quadratic fit to the experimental data. It is observed that the classical diffusion T decreases linearly with the sample thickness and the experimental results shows quadratic dependence $T \propto L^{-2}$. This is an expected behaviour for the localization transition. Fig. 7 shows the transmission coefficient as a function of sample thickness. The data are plotted on a double logarithmic scale. It shows the exponential decay behaviour. From this result we expect stronger scattering behaviour of the particles. The solid line shows exponential fit $\exp(-L/l_{loc})$. The $l_{loc}$ obtained is nearly 225nm.

**Conclusion**

In conclusion we have experimentally observed weak localization of light in gold nanofluid synthesized using marine derived fungus *Aspergillus niger*. This is the first backscattering report for the *Aspergillus niger* synthesized gold nanoparticles. The TEM and observed single peak in UV-vis spectra shows the spherical nature of the synthesized gold nanoparticles. The coherent backscattering experiment was carried out for the two particle size (15nm and 35 nm) of gold nanoparticles in aqueous suspension. It is observed that $1<kl^*<5$. Further the $kl^*$ is inversely proportional to the size of the gold nanoparticles and width of the backscattering cone is also inversely proportional to the $kl^*$. In the total transmission experiment a quadratic scaling is obtained using $T \propto L^{-2}$ and the localization length $l_{loc}$ obtained from the theoretical fit $\exp(-L/l_{loc})$ is nearly 225 nm.

**Acknowledgement**

The work was carried out with financial support sanctioned under CSIR's Scientists' Pool scheme to AKV (Pool No. 8426-A). The Department of Science and Technology (DST), Govt. of India, New Delhi is also acknowledged for financial support. AKV acknowledges DST for

providing financial support under Women Scientists' Scheme (WOS-A). RP is thankful to DST for providing financial support in terms of project SB/S2/CMP-022/2014.

**References**

1 N. Savage, "Trick of light", *Nature*,2013, **495**, S8

2 J. Yang Jingbi You, Chun-Chao Chen, Wan-Ching Hsu, Hai-ren Tan, Xing Wang Zhang, Ziruo Hong, and Yang Yang, "Plasmonic Polymer Tandem Solar Cell", *ACS Nano*, 2011, **5**, 6210-6217

3 J.-S Bouillard, S. Vilain, W. Dickson , G. A. Wurtz , A. V. Zayats, "Broadband and broadangle SPP antennas based on plasmonic crystals with linear chirp", *Sci. Rep.*,2012, **2**, 829

4 M. Han, X. Gao, J. Z. Su, S. Nie, "Quantum-dot-tagged microbeads for multiplexed optical coding of biomolecules". *Nat. Biotechnol.*2001, **19**, 631–635.

5 Anh D. Phan, Trinh X. Hoang, Thi H. L. Nghiem, and Lilia M. Woods, "Surface plasmon resonances of protein-conjugated gold nanoparticles on graphitic substrates", *Appl. Phys. Lett.,* 2013, **103**, 163702

6 Jinhua Li, Huaijuan Zhou, Shi Qian, Ziwei Liu, Jingwei Feng, Ping Jin, and Xuanyong Liu, "Plasmonic gold nanoparticles modified titania nanotubes for antibacterial application", *Appl. Phys. Lett.,*2014, **104**, 261110

7 A. K. Salem, P. C. Searson, K. W. Leong, "Multifunctional nanorods for gene delivery". *Nat. Mater*. 2003, **2**, 668–671.

8 Rakesh Singh Moirangthem, Mohammad Tariq Yaseen, Pei-Kuen Wei, Ji-Yen Cheng, and Yia-Chung Chang, Enhanced localized plasmonic detections using partially-embedded gold nanoparticles and ellipsometric measurements, *Biomed Opt Express*.2012, **3(5),** 899–910.

9 Kathryn M. Mayer†,§ and Jason H. Hafner, *Chem. Rev.,* 2011, **111**, 3828–3857

10 Sabine Szunerits*, Jolanda Spadavecchia and Rabah Boukherroub, *Rev Anal Chem* 2014; **33(3)**: 153–164

11 Yeonee Seol, Amanda E. Carpenter, and Thomas T. Perkins, Gold nanoparticles: enhanced optical trapping and sensitivity coupled with significant heating, *Opt. Lett.*, 2006, **31,** 2429-2431

12 P. Sheng, *Introduction to Wave Scattering, Localization and Mesoscopic Phenomena*, (Academic, San Diego, 1995]

13 M. Segev, Y. Silberberg, D. N. Christodoulides, "Anderson Localization of Light", *Nat. Photon*., 2013**, 7**, 197-204,

14 E. Akkermans, P. E. Wolf, R. Maynard, "Coherent Backscattering of Light by Disordered Media: Analysis of the Peak Line Shape", *Phys. Rev. Lett.*,1986, **56**, 1471-1474

15 P. E. Wolf, G. Maret, "Weak Localization and Coherent Backscattering of Photons in Disordered Media", *Phys. Rev. Lett,*1985, **55**, 2696-2699

16 M. P. Van Albada, Ad Lagendijk, "Observation of Weak Localization of Light in a Random Medium", *Phys. Rev. Lett.*,1985, **55**, 2692-2695

17 D. S. Wiersma, P. Bartolini, Ad Lagendijk, R. Righini, "Localization of light in a disordered medium", *Nature*,1997, **390**, 671-673

18 R. Sapienza, S. Majumdar, C. Cheung, A. G. Yodh, D. Wiersma, "Anisotropic weak localization of light", *Phys. Rev. Lett.*,2004, **92**, 033903

19 M. Gurioli, F. Bogani, L. Cavigli, H. Gibbs, G. Khitrova, D. S. Wiersma, "Weak localization of light in a disordered microcavity", *Phys. Rev. Lett.*,2005, **94**, 183901

20 M. Burresi, V. Radhalakshmi, R. Savo, J. Bertolotti, K. Vynck, D. Wiersma, "Weak localization of light in superdiffusive random system", *Phys. Rev. Lett.*, 2012, **108**, 110604

21 Diederik S. Wiersma, Meint P. van Albada, Bart A. van Tiggelen, and Ad Lagendijk, "Experimental Evidence for Recurrent Multiple Scattering Events of Light in Disordered Media", *Phys. Rev. Lett.*, 1995, **74**, 4193-4196

22 J. Huang, N. Eradat, M. E. Raikh, and Z. V. Vardeny, A. A. Zakhidov and R. H. Baughman "Anomalous Coherent Backscattering of Light from Opal Photonic Crystals", *Phys. Rev. Lett.*, 2001, **86**, 4815

23 Y. Bidel, B. Klappauf, J. C. Bernard, D. Delande, G. Labeyrie, C. Miniatura, D. Wilkowski, and R. Kaiser, "Coherent Light Transport in a Cold Strontium Cloud", *Phys. Rev. Lett.*, 2002, **88,** 203902

24 N. Hogan, A. Urban, C. A. Orozco, A. Pimpinelli, P. Nordlander, N. Halas, "Nanoparticles heat through light localization", *Nano Lett.*, 2014, **14 (8)**, 4640–4645.

25 A. K. Vala "Investigations on Gold Nanoparticles Biosynthesis Potential of Marine Derived Fungi", *BioTechnology : An Indian Journal,* 2014, **9(5),** 206 – 209

26 A. K. Vala "Exploration on green synthesis of gold nanoparticles by a marine derived fungus *Aspergillus sydowii*", Env Prog & Sustain Energy 2015, **34(1),** 194-197; DOI 10.1002/ep.11949

27 S. Iravani and B. Zolfaghari. "Green Synthesis of Silver Nanoparticles Using *Pinus eldarica* Bark Extract", *BioMed Research International Volume,* 2013, Article ID 639725, http://dx.doi.org/10.1155/2013/639725

28 R. Sanghi, P. Verma. "pH dependant fungal proteins in the 'green' synthesis of gold nanoparticles". *Adv. Mater. Lett.* 2010, **1(3)**, 193-199

29 A. K Mittal, A. Kaler, A V. Mulay, and U. C. Banerjee. "Synthesis of Gold Nanoparticles Using Whole Cells of *Geotrichum candidum". Journal of Nanoparticles,* 2013, Article ID 150414,. http://dx.doi.org/10.1155/2013/150414

30 S. K. Das, J. Liang, M. Schmidt, F. Laffir, E. Marsili, "Biomineralization mechanism of gold by zygomycete fungi *Rhizopous oryzae". ACS Nano.* 2012, **6**, 6165–6173.

31 G. Mie, "Beitrage zur optik truber medien". *Annalen der Physik (Leipzig)*, 1908, **25(3)**, 377–445.

32 M. Kaveh, M. Rosenbluh, I. Edrei, and I. Freund, "Weak Localization and Light Scattering from Disordered Solids", *Phys. Rev. Lett.*, 1986, **57**, 2049-2052

Table-1. The parameters obtained from the backscattering experiment for the two particle size of the gold nanoparticles are transport mean free path l*, scattering mean free path l, backscattering cone width w, and localization parameter kl*.

| d (nm) | l*(μm) | l (nm) | w(mrad) | Kl* |
|---|---|---|---|---|
| 15 | 0.292 | 20.44 | 4.29 | 2.9 |
| 35 | 0.161 | 11.27 | 5.45 | 1.5 |

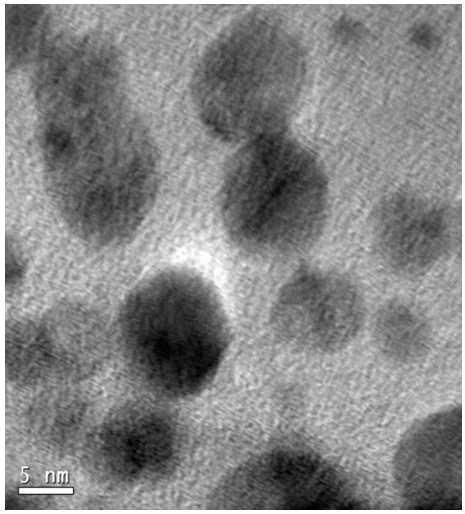


Fig.1 shows the typical TEM image of the gold nanoparticles synthesized using marine derived fungus Aspergillus Niger

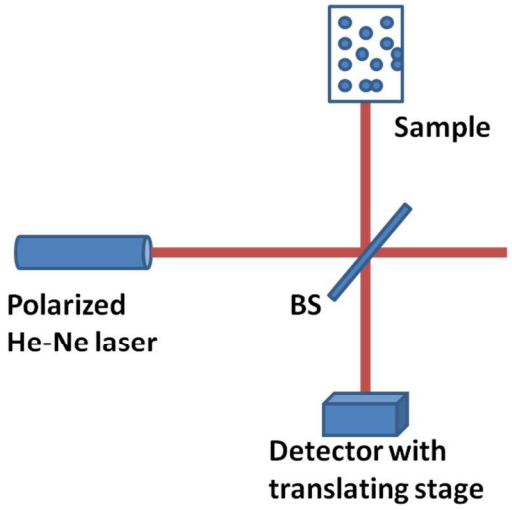


Fig.2. Schematic representation for the backscattering experimental set up.

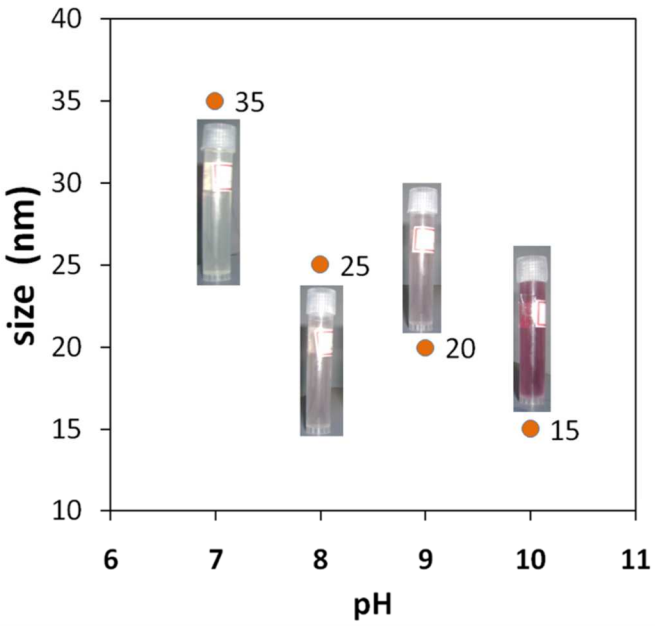


Fig.3 shows the pH dependent size variation in the biosynthesized gold nanoparticles and its solution color in the day light. The size decreases as the color becomes dark pink.

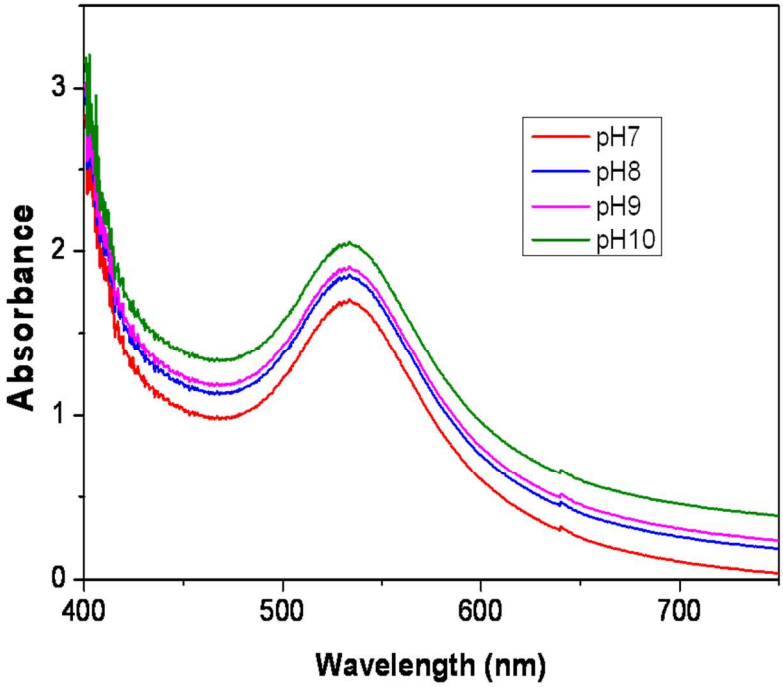


Fig.4. shows UV-vis spectra for the biosynthesized gold nanoparticles using marine derived fungus Aspergillus niger. The peak is the characteristic peak for the gold nanoparticles around 540 nm wavelength.

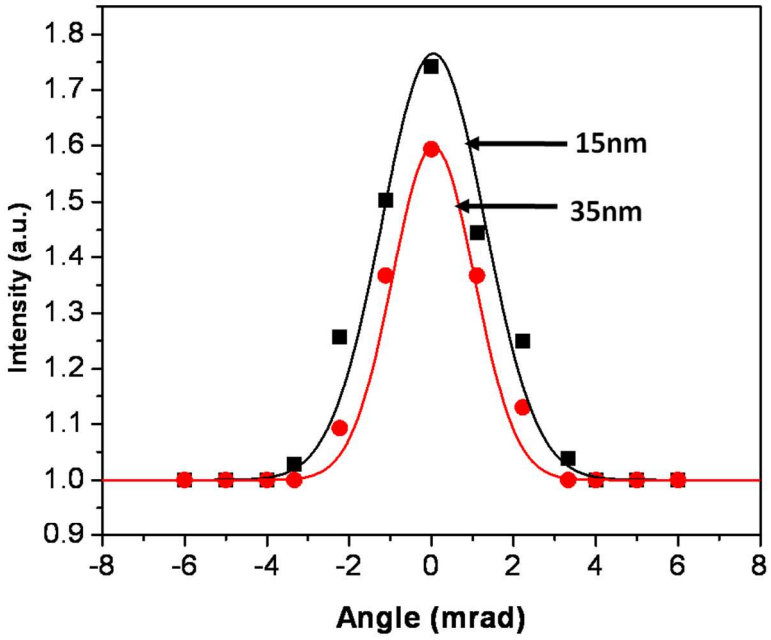


Fig.5 shows the backscattering cone as a function of angle for the two particle size 15 and 35 nm of gold particles synthesized using marine derived fungus Aspergillus niger.

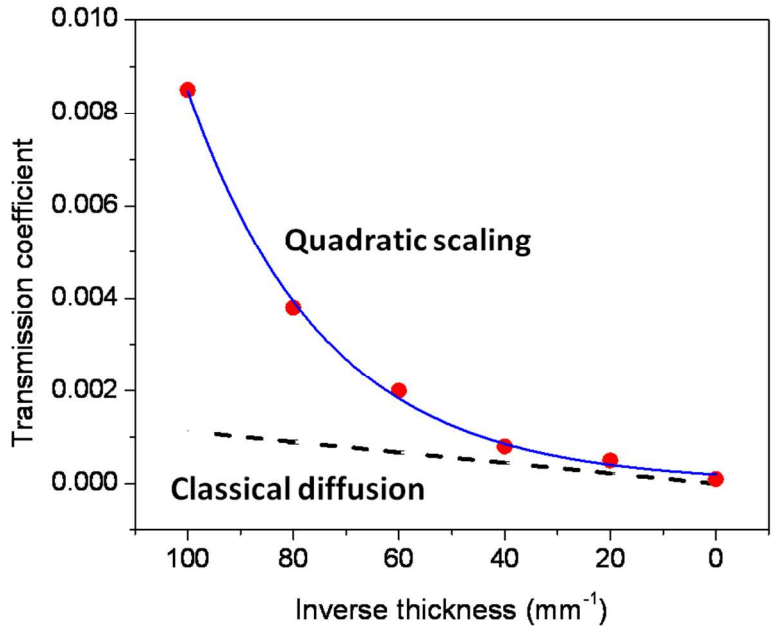


Fig.6 shows the transmission coefficient as a function of inverse sample thickness. The dashed line shows the classical diffusion with l = 11.27 nm. The solid line, fit to the experimental results shows the quadratic fit, exhibits the localization transition.

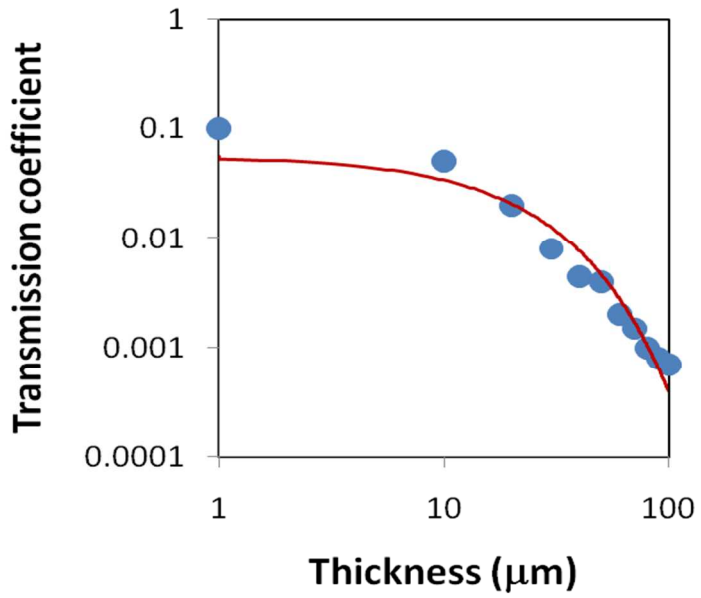


Fig. 7 shows the log-log plot of transmission coefficient as a function of sample thickness for the 35 nm gold particles. It shows the exponential decay $\exp(-L/l_{loc})$. The $l_{loc}$ obtained from the same is 225 nm.