

Discrete dipole approximation studies of silver nano crystals in sol-gel silica

J. JOHN¹, V. THOMAS^{1,2,*}, R. G. S. SOFIN², P. R. R. KUMAR³, T. T. FERNADEZ⁴, H. THOMAS¹, G. JOSE⁵, N. V. UNNIKRISHNAN⁶, R. L. THOMAS⁷

¹Department of Physics, Christian College Chengannur-689122, University of Kerala, India.

²Department of Physics, College of Science, Sultan Qaboos University, AlKhoud, Oman.

³Department of Physics, S.N.College, Kollam, University of Kerala, India.

⁴Instituto de Óptica, CSIC, Madrid, España.

⁵Institute for Materials Research, School of Process, Environmental and Materials Engineering, University of Leeds, UK.

⁶School of Pure and Applied Physics, Mahatma Gandhi University, Kottayam-686560, India.

⁷Department of Physics, St. Joseph's College for Women, Alappuzha, University of Kerala, India

Silver nanoparticles have garnered appreciable attention because of their distinctive characteristics that result from the stimulation of surface plasmon resonance (SPR). They are very much successful commercially, due to their excellent conductivity, chemical stability, catalytic activity, and antibacterial activity. In this work we are presenting, silver nanocrystals (AgNCs) doped silica glassy materials prepared using sol-gel technique. The formation of silver nanocrystals was confirmed by X-ray diffraction (XRD) and high-resolution transmission electron micrograph (HRTEM). Further studies prove Surface plasmon resonance (SPR) of AgNCs in the system between the wavelength range 350-470nm. Numerical calculation of SPR of AgNCs with spherical morphology was also done on the basis of discrete dipole approximation (DDA).

(Received January 31, 2023; accepted October 6, 2023)

Keywords: Surface plasmon resonance, DDA, Sol-gel glasses

1. Introduction

Porous silica materials made by low-temperature sol-gel process are promising host matrixes for rare earth ions, transition metal ions, noble metals, nanocrystals and biomolecules [1-5]. Nano particles prepared by doping noble metals in sol gel silica exhibit a behavior significantly different from that of its bulk counterpart [6]. Plasmonic properties of silver nanoparticles (AgNPs) have been widely studied for their superior performances that exceed those of other metals with a surface plasmon resonance (SPR) in the visible range like gold or copper [7]. Up until recently, a number of applications based on the SPR of AgNPs have been presented, in particular for biosensing, surface-enhanced Raman scattering and plasmon circuitry. Most of these applications take advantage of the engineering of AgNP's plasmonic response that depends on their size, shape, dielectric environment and on mutual electromagnetic interactions among particles in close proximity [8].

The important feature of nano plasmonic phenomena is the combination of a strong spatial localization and high-frequency (from ultraviolet to infrared) of electron oscillations. The plasmon nanoparticles are proposed to be used in nano lasers and to stimulate plasmonic oscillations in nanoparticles by means of the optical emission. Very often, the numerical studies do not allow one to explain the physics of the observed phenomena, while the analytical studies are mostly devoted to the case of spherical and

spheroidal nanoparticles, which are very far from the synthesized nanostructures from the viewpoint of geometry and physics. Moreover, the physics of plasmonic oscillations in complex nanostructures and nanoparticles remains insufficiently studied, and to make progress in this field one should use new approaches and ideas. In this work, we have used the DDA [9] for studying the SPR of spherical AgNP's in silica glassy materials.

2. Experimental

Samples with 0.04 % (mol%) silver in silica glasses were prepared through sol-gel route. Tetraethyl orthosilicate (TEOS) was used as the precursor for the base silica glass. Water was used for the hydrolysis and ethanol as the solvent. Silver nitrate was used for doping the required amount of ions into the silica. The final mixture was stirred for 30 minutes to ensure the homogeneity of the solution before casting. The solvent was cast into polypropylene containers and sealed and kept undisturbed in a dark place for several days for the formation of the gel. Later the gel was heat treated to 600°C in a programmable furnace operating at a heating rate of 1°C/minute. We have taken low concentration of silver to avoid agglomeration and cluster formation of nanoparticles which in turn results in the formation of other structures like icosahedral, ellipsoidal, cylindrical etc [10]. The samples were characterized using a spectrophotometer (Shimadzu-UVPC

2401), transmission electron microscope (FEI Quanta FEG 200).

3. Results and discussion

Fig. 1 shows the XRD spectra of silver nano crystals doped sample. The peaks are identified to be arising from the nanocrystals of silver. With the help of JCDPS card number 04-0783 the peaks were identified. The particle size was calculated by employing Debye-Scherrer formula [10]. Size of the crystal was found to be 21 nm. Since the nano crystals are embedded in silica matrix, the possibility of strain factor could not be ruled out, but the calculated strain factor was found to be negligible [10].

To confirm the crystallite, size the transmission electron microscopy was taken and is in well agreement with the values calculated using the Debye-Scherrer formula. Fig. 2 shows the TEM image obtained. Inset of the image show the electron diffraction pattern and the crystallite size distribution of the respective sample. The growth of particle size of silver in silica matrix depends mainly on the diffusion coefficient, activation energy of

coalescence, heat treatment time and temperature of the matrix [11].

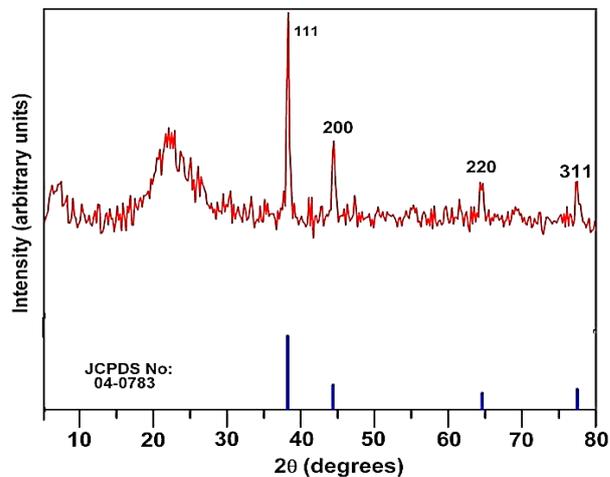


Fig. 1. XRD spectra of silver doped sample in comparison with the JCPDS data (color online)

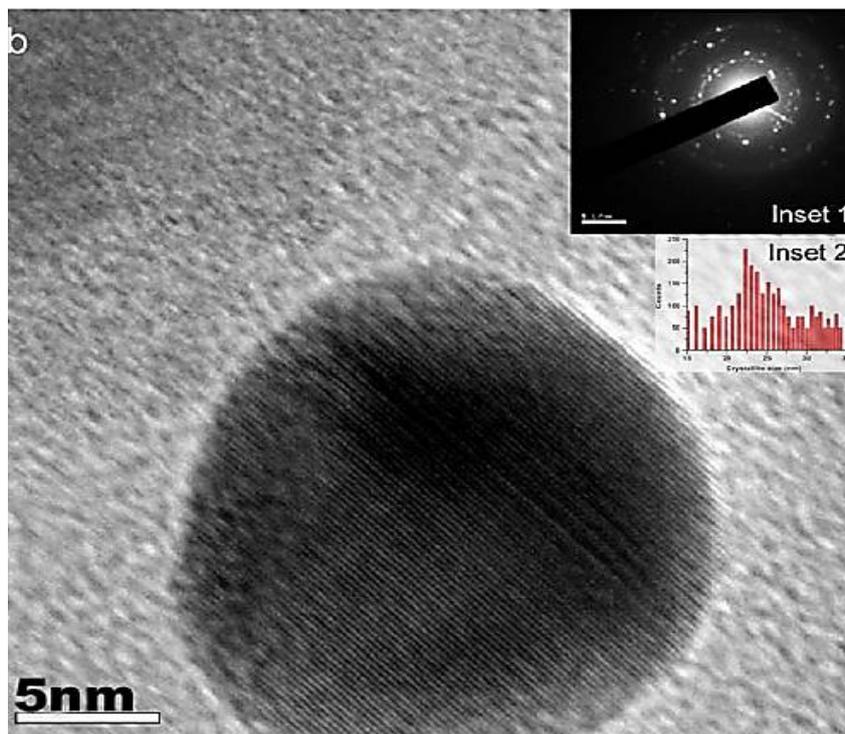


Fig. 2. Transmission electron microscope image of silver doped sol-gel silica Inset-1: corresponding electron diffraction pattern; Inset-2: corresponding particle size distribution (color online)

The absorption spectra of AgNCs in vacuum, experimental absorption spectra and calculated absorption spectra of AGNCs in SiO_2 are presented in Fig 3(A), 3(B) and 3(C) respectively. Strong absorption in the 350-470nm region represents the SPR absorption of AGNCs. Broadening of the Plasmon band along with a redshift in peak position was observed compared to plasmon resonance in air [12].

The intense absorption band is due to the collective oscillation of all free electrons in the silver particles resulting from the interaction with electromagnetic radiation. This collective oscillation of conduction electrons in metals are known as “plasmons”. According to the Fermi liquid model plasmons can be satisfactorily described as a negatively charged electron cloud displaced from its equilibrium position around a lattice made of positively

charged ions, in analogy to a real plasma. The characteristic oscillation frequency is given by,

$$\omega_p = \sqrt{\frac{Ne^2}{\epsilon_0 m_e}} \quad (1)$$

where ω_p is the plasma frequency, N is the conduction electron density, e is the electronic charge, m_e is the electron effective mass and ϵ_0 is the vacuum dielectric permittivity [8].

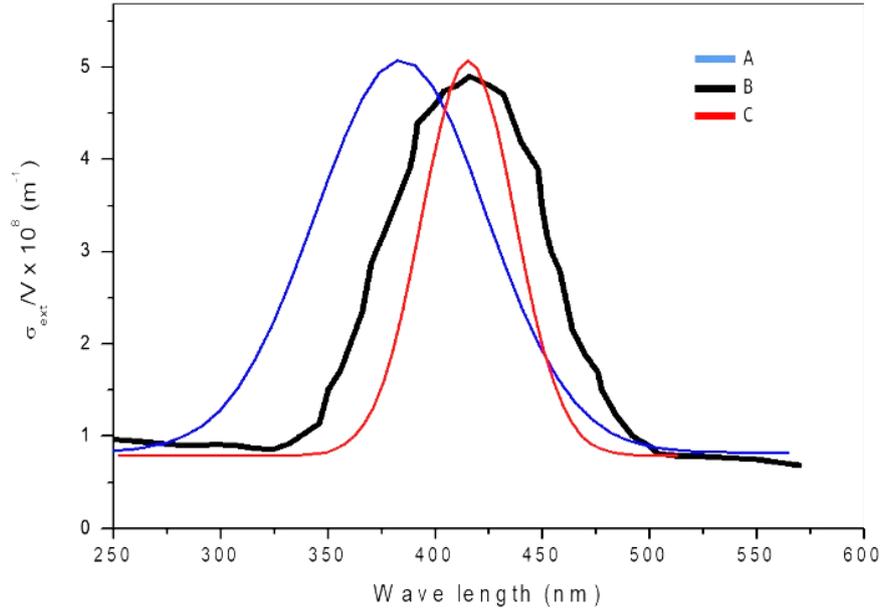


Fig. 3. Light absorbance of AgNPs, DDA vs experimental data (A- DDA spectrum for AgNPs in vacuum, B- Experimental spectrum (0.04%), C-DDA spectrum for AgNPs in SiO₂) (color online)

The SPR of AGNCs with high symmetry can be calculated with good accuracy by the Mie theory [13]. Mie theory is not very reliable when the particle symmetry is lowered. One of the most reliable numerical methods for the calculation of SPR is the discrete dipole approximation (DDA) developed by Draine and co-workers [9,14]. The results of DDA are reliable if the nanoparticles are described with an adequate number of dipoles and with adequate size corrected dielectric constant. In DDA the nanostructure is represented by a cubic array of N cubic dipoles. Discrete structure of the target is the only limitation in DDA analysis [15]. The polarization P_j induced on each point j of position r_j and polarizability α_j is given by

$$\vec{P}_j = \alpha_j \vec{E}_{Loc}(\vec{r}_j) \quad (2)$$

where E_{Loc} is the electric field originated by the incident radiation of all other dipoles

$$\vec{E}_{Loc}(\vec{r}_j) = \vec{E}_0 \exp(i\vec{k} \cdot \vec{r}_j + i\omega t) - \sum_{i \neq j} \vec{A}_{ji} \vec{P}_i \quad (3)$$

where \vec{E}_0 is the incident electric field, $k = \omega/c$ is the wave vector and \vec{A}_{ji} is the interaction matrix. The full expression of \vec{A}_{ji} is

$$\vec{A}_{ji} = \frac{\exp(i\vec{k} \cdot \vec{r}_{ji})}{r_{ji}^3} \times \left\{ k^2 \vec{r}_{ji} \times (\vec{r}_{ji} \times \vec{P}_i) + \frac{(1 - ik\vec{r}_{ji})}{r_{ji}^2} \left[\vec{r}_{ij} \vec{P}_i - 3 \vec{r}_{ji} (\vec{r}_{ji} \cdot \vec{P}_i) \right] \right\} \quad (4)$$

The base of DDA is characterized by the way in which α_j is expressed. In the present case we have employed the MATLAB program for obtaining the DDA spectra corresponding to AGNCs having an average size of 20nm. The calculated absorption spectrum of AGNCs (Fig 3(C)) in silica shows a redshift and broadening. The full width half maximum (FWHM) of calculated SPR spectrum in air

is found greater than that in the medium. This variation in FWHM of SiO₂ is due to the effect of dielectric material on SPR [16]. According to the effective medium theory developed by Maxwell and Garnett, when AGNCs are incorporated in SiO₂ matrix, AgNCs- dielectric medium system could be replaced with a homogeneous material exhibiting the same dielectric polarization upon

electromagnetic interaction [17]. Including this, the complex dielectric function can be written as

$$\frac{\epsilon_{eff} - \epsilon_m}{\epsilon_{eff} - 2\epsilon_m} = f \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \quad (5)$$

Hence, the extinction crosssection takes the form

$$\alpha(cm^{-1}) = \frac{8.88 \times 10^7}{\lambda(nm)} \sqrt{-\epsilon_{1eff} + \sqrt{\epsilon_{1eff}^2 + \epsilon_{2eff}^2}} \quad (6)$$

In short, all these interactions will lead to redshift and change in FWHM without affecting the position of the surface plasmons.

4. Conclusions

In the present work, we have prepared silver nano crystals doped silica glasses via sol – gel route. Formation of silver nanocrystals was confirmed by XRD and HRTEM. Using Debye-Scherrer formula average crystalline size was calculated to be 21nm. HR-TEM images also confirmed the above crystalline size obtained from XRD. The surface plasmon resonance (SPR) of silver nanoparticles was observed in the wavelength range 350-470nm. Numerical calculation of SPR based on DDA confirms the validity of the method.

Acknowledgements

Authors (NVU and VT) are thankful to University Grants Commission (UGC, Government of India) for financial assistance.

References

- [1] Vinoy Thomas, Gin Jose, Gijo Jose, P. I. Paulose, N. V. Unnikrishnan *Mat. Chem. Phys.* **77**, 826 (2003).
- [2] Gijo Jose, Vinoy Thomas, Gin Jose, Cyriac Josphe, M. A. Ittyachen, N. V. Unnikrishnan, *Mat. Chem. Phys.* **96**, 381 (2006).
- [3] Vinoy Thomas, Gin Jose, Gijo Jose, P. R. Biju, N. V. Unnikrishnan, *J. Sol-Gel Sci. Tech.* **33**, 105 (2005).
- [4] C. J. Brinker, G. W. Scherer, *Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing*, Academic Press, New York, 1990.
- [5] Padmaja Parameswaran Nampia, Cheranellore Chandrasekharan Karthab, Gin Jose, P. R. Anil Kumar, Thapasimuthu Anilkumara, Harikrishna Varmaa, *Sensors and Actuators B* **185**, 252 (2013).
- [6] Oleg A. Yeshchenko, Igor M. Dmitruk, Alexandr A. Alexeenko, Mykhaylo Yu. Losytskyy, Andriy V. Kotko, Anatoliy O. Pinchuk, *Phys. Rev. B* **79**, 235438 (2009).
- [7] Nikolai G. Khlebtsov, Lev A. Dykman, *J. Quant. Spectr. Rad. Tra.* **111**, 1 (2010).
- [8] J. Ren, R. D. Tilley, *J. Amer. Chem. Soc.* **129**, 3287 (2007).
- [9] F. T Draine, D. J Flatau, *J. Opt. Soc. Amer. A* **11**, 1491 (1994).
- [10] P. R. Rejikumar, P. V. Jyothy, Siby Mathew, Vinoy Thomas, N. V. Unnikrishnan, *Physica B* **405**, 1513 (2010).
- [11] Gijo Jose, Vinoy Thomas, Gin Jose, Cyriac Josphe, M. A. Ittyachen, N. V. Unnikrishnan, *J. Fluorescence* **14**, 733 (2004).
- [12] C. Noguez, *J. Chem Phys.* **111**, 3806 (2007).
- [13] A. Pinchuk, U. Kreibig, A. Hilger, *Surface Science* **557**, 269 (2004).
- [14] B. J Draine, J Goodman, *J. Astrophys.* **405**, 685 (1993).
- [15] Vincenzo Amendola, Osman M. Bakr, Francesco Stellacci, *Plasmonics* **5**, 85 (2010).
- [16] Mahmoud A. Mahmoud, Maysamreza Chamanzar, Ali Adibi, Mostafa A. El-Sayed *J. Am. Chem. Soc.* **134**, 6434 (2012).
- [17] M. A. Garcia, *J. Phys. D: Appl. Phys.* **44**, 283001 (2011).

*Corresponding author: vinoythoma@gmail.com