Surface Plasmon Resonance



Study of Tunable Plasmonic, Photoluminscence, and Nonlinear Optical Behavior of Ag Nanoclusters Embedded in a Glass Matrix for Multifunctional Applications

Promod Kumar,* Mohan C. Mathpal, Jai Prakash, Syed Hamad, Soma Venugopal Rao, Bennie C. Viljoen, Mart-Mari Duvenhage, Eric G. Njoroge, Wiets D. Roos, and Hendrik C. Swart*

Plasmonic based hybrid noble metal nanoclusters (NCs) have gained much interest in various technological applications such as optoelectronics, photonic devices and nonlinear media including biomedical applications due to their tunable optical properties. Here, Ag NCs are grown as embedded in glass using simple ion-exchange process and effect of various parameter including post thermal treatment is studied on tunability of their optical behavior (plasmonic, optical nonlinearity, and photoluminescence properties) in view of their potential applications in nanophotonics devices and as nonlinear media. The tunable optical, structural and thermodynamic properties associated with the rapid growth and agglomeration of Ag NCs in the glass is also studied under the post thermal treatment process. The various techniques such as XRD, RBS, Z-scan and UV-vis, XPS, PL and TEM are used for characterizing ion exchanged samples. A blue shift of 15 nm is observed significantly in optical absorbance as a function of post thermal treatment. Open and closed aperture Z-scan experiments show strong nonlinear absorption coefficients for the Ag NCs. The thermodynamic parameters such as enthalpy (Δ H), entropy (Δ S) and Gibbs energy (Δ G) for the nucleation and growth of the Ag NCs in the glass matrix are calculated at different temperatures with an activation energy of 59 kJ mol⁻¹ obtained by the Arrhenius linear equation and a model is suggested. In addition, these Ag NCs embedded glasses exhibit good antimicrobial activities (against E. coli bacteria) with a change in antibacterial behavior at higher annealing temperature indicating their multifunctional applications.

1. Introduction

The development of new plasmonic based hybrid noble metal nanostructures with higher stability, controllability and tunable optical properties becomes an important challenge in the modern age of fast growing technology. It could be possible by the use of nanotechnology. Plasmonic based hybrid noble metal nanostructures especially those designed for photonics have attracted researcher over the last decades and now become an emerging field of nanophotonics. Large third order nonlinearities have been observed in metal nanoclusters (NCs) embedded glass matrices. Plasmonic metal NCs are promising compared to other NCs from the surface plasmon resonance (SPR) viewpoint.^[1,2] The unique nonlinear optical (NLO) behavior of plasmonic metal NCs can be accredited to their SPR bands. These plasmonic NCs^[3-8] in different matrices have been proved to be attractive for their large NLO coefficients. Generally, silver nanoparticles (NPs) have been studied extensively because they exhibit a broad absorption spectral region in the 400-

Dr. P. Kumar, Dr. J. Prakash, Dr. M.-M. Duvenhage, Prof. W. D. Roos, Prof. H. C. Swart Department of Physics University of the Free State Bloemfontein ZA9300, South Africa E-mail: pkpmcm@gmail.com; talk2promodthakur@gmail.com; swarthc@ufs.ac.za Dr. M. C. Mathpal Department of Physics Universidade de Brasília Brasilia, DF, Brazil-70910900 Dr. J. Prakash

Department of Chemical Engineering Indian Institute of Technology Kanpur Kanpur-208016, India

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Dr. I. Prakash Institut National de la Recherche Scientifique-Énergie Matériaux et Télécommunications (INRS-EMT) Quebec, J3×1S2, Canada Dr. S. Hamad, Prof. S. V. Rao Advanced Centre for Research in High Energy Materials (ACRHEM) University of Hyderabad Telangana, India Prof. B. C. Viljoen Department of Microbial Biochemical and Food Biotechnology University of the Free State Bloemfontein, ZA 9300, South Africa Dr. E. G. Njoroge ENGAGE University of Pretoria Pretoria 0002, South Africa





700 nm spectral range. These properties have affinity to generate strong surface plasmons and this could be due to the possibility of less s-d hybridization. This s-d hybridization influences to minimize the strength of dipole oscillations which are minimal in the case of Ag NCs when compared with Au NCs.^[9–11] Therefore, the Ag NPs are more favorable to depict high third order nonlinearities. Thus far, very few researchers have shown the presence of large nonlinearities in Ag NCs embedded glasses achieved by various physical methods. Specifically, Mai et al.^[12] demonstrated both reverse saturable absorption (RSA) and saturable absorption (SA) behavior with large nonlinear optical coefficients for Ag NPs/clusters dispersed in a transparent oxyfluoride glass matrix at a 480 nm wavelength with nanosecond pulses and utilizing the Z-scan technique.

Similarly, Karthikayen et al.^[13] reported the NLO absorption in Ag NCs with varying sizes from 2 to 6 nm, embedded in a glass matrix. They also reported a transition from SA to pure RSA in both picosecond and femtosecond domains. Similar behavior has been reported in case of Au NPs in different matrices such as silica glass,^[14,15] the SiO₂-TiO₂ matrix.^[16] Plasmonic materials based hybrid noble metal nanostructures with fast nonlinearities near the SPR frequencies with a picoseconds range and ultrafast response are generally considered as a suitable candidates for the various applications such as ultrafast switching, optical communication, optical information processing, optical data storage and optical limiting applications.^[17–22] The NLO response of glass materials containing plasmonic metal NCs have attracted considerable attention due to its high polarisability and ultrafast nonlinear response which can be utilized in making all optical switching devices. In particularly, plasmonic metal NCs incorporated into glass matrix are well known as most suitable and promising materials in order to detect the enhancement in optical properties by SPR due to its fast nonlinearities susceptibility and ultrafast response properties.^[23,24] In this context, such glasses are fabricated by incorporating the desired noble metals into a favorable dielectric host such as glass materials, followed by the metal reduction that can be achieved by a thermal annealing process in inert as well as oxidized atmosphere. Soda-lime glass generally acts as an excellent host for growing metal NCs in a desirable shape and size because of its essentials characteristics such as good homogeneity, chemical stability, transparency and preventing the air oxidation of noble metal nanoparticles. The metallic NCs incorporated into a glass matrix can be produced by several methods including thermal treatment, irradiation using UV, gamma followed by post thermal treatment, producing a very narrow size range of NCs.[20]

Ag ions doped in the glass host materials can be produced by spray pyrolysis, melt-quench, ion implantation, and sputtering technique or a simple ion-exchange process. The ion-exchange combined with post thermal treatment is probably the most suitable and simple method to incorporate metal NCs in the glass host materials along with very cost effective.^[18,19]

In the present work, the Ag NCs were incorporated into a glass matrix by a simple ion-exchange porcess followed by annealing at different temperatures for the rapid growth and the agglomeration of Ag atoms. The structural, optical (plasmonic, optical nonlinearity, and photoluminescence properties) and antimicrobial properties along with thermodynamic behavior of the thermally annealed samples have been discussed and explained with their mutual thermodynamic parameters. The nonlinear absorption of Ag NCs dispersed in the glass matrix has been studied by Z scan techniques using 800 nm nanosecond laser light and nonsaturated and saturated nonlinear absorption behaviors have been discussed. The thermodynamic parameters are generally required to find the thermodynamic aspects for the thermally induced growth mechanism of metals by considering the enthalpy, entropy and Gibbs energy. In this context, thermally induced parameters are logically coordinated with thermodynamic calculations involving metal dispersed glass fabrication which have been discussed here in the formation of Ag NCs. This is also interesting to study the antimicrobial behavior of Ag NCs embedded in glass matrix which is of potential applications in biomedical field.^[25,26] Therefore, the present work has also been explored to study the mechanism of antimicrobial action of Ag NCs embedded in the glass matrix.

2. Experimental Details

2.1. Sample Preparation

Ag ions were incorporated into glass host materials through the $Na^+ \leftrightarrow Ag^+$ simple ion exchange techniques combined with post thermal treatment in an oxidized atmosphere at different temperatures. Commercial glass slides with composition (in weight %) of 72.0% SiO₂, 14.0% Na₂O, 0.6% K₂O, 7.1% CaO, 4.0% MgO, 1.9% Al₂O₃, 0.1% Fe₂O₃, 0.3% SO₃) of 0.5 mm thickness were purchased from "MARIENFELD" a German make company for the simple ion exchange (Na⁺ \leftrightarrow Ag⁺) experiment. The glass slides were ultrasonically cleaned for 2 h using distilled water, methanol and acetone to remove the glass surface impurities. The glass slides were dipped in the molten salt bath of 3 mol% AgNO3 in a NaNO3 mixture and heated at 390 °C for 5 min. The Ag ions in the salt bath were incorporated into the glass matrix by replacing the alkali Na⁺ ions in the glass matrix. The Ag pristine samples were cooled and removed from the molten bath after inter-diffusion and washed with water and acetone once again to remove the glass surface impurities during the ion exchange process. The obtained Ag pristine glass samples were colorless or slight yellow after inter-diffusion. The Ag pristine samples were thermally treated at various temperatures from 450 to 650 °C for 1 h in an oxidized atmosphere to induce the nucleation and growth of the Ag in the glass matrix. Energy is needed to move the ions towards the relaxed glass surface. A higher concentration of Ag atoms aggregated on the surface and the diffusion was obtained on the glassy surface after heating the samples at the higher temperatures and it could be understood by the different ionic radius ratio of Ag⁺ and Na⁺, $r_{\rm Ag+}/r_{\rm Na+}$ is 1.29.^[27,28]

2.2. Characterization

Synthesized Ag pristine samples and thermally treated samples at different temperatures were characterized using a Bruker D8 X-ray diffractometer (XRD) to study the crystalline nature of the post annealed Ag glass samples. The XRD was operated at 40 kV





and 40 mA with a wavelength of 0.1540 nm and the samples were scan in the range of $20^\circ\text{--}80^\circ,$ respectively.

The plasmonic behavior of the Ag NCs diffused in the glass matrix were studied using UV-visible absorption in the wavelength range of 300–800 nm and the absorbance mode were carried out on the samples using a Lambda 950 UV – Vis-NIR spectrophotometer with an integrating sphere from PerkinElmer. A pure glass slide was used as the reference prior for the UV measurements.

The Ag thermally annealed samples was characterize using A JEOL JEM 2100 ultra-high resolution field emission gun electron microscope (FEGTEM) operated at 200 kV. Photoluminescence (PL) studies of the samples were carried out using a Flouromax Photoluminescence spectrophotometer.

X-ray photoelectron spectroscopy (XPS) were used to study the chemical state of the Ag doped glass samples after the thermal treatment at various temperatures. The XPS analyses were carried out with a PHI 5400 XPS spectrometer using a nonmonochromatic Mg K_a X-ray source (1253.6 eV, 15 kV, 200 W) and hemispherical sector analyzer. The work function of the instrument was calibrated using a binding energy (BE) of 83.96 eV for the Au $4f_{7/2}$ peak and adjusting the linearity of the energy scale to give a BE of 932.67 eV for the Cu 2p_{3/2} peak. The photoelectron take-off angle for all measurements was 45°. Survey scans were done with a pass energy of 178.95 eV in energy steps of 0.25 eV and dwell time of 100 ms. High resolution scans used a pass energy of 44.75 eV and step size 0,125 eV. Charge correction was done by correcting to the C-C bond at a binding energy of 284.8 eV. The XPS high resolution spectra were analyzed using XPS PEAK 4.1 software. Rutherford backscattering spectrometry (RBS) measurements were carried out using a 2 MeV He ion beam. The incident beam was normal to the glassy sample surface, and scattered clusters were collected at the angle of 165 °C. In brief UV, PL, XRD, RBS, XPS, and TEM have been mainly studied to understand the formation mechanism of the Ag NCs in the glass matrix. The antibacterial activity of the Ag NCs was determined by means of the disk diffusion assay method using Escherichia coli (ATCC 33985) as an indicator microorganism. E. coli was cultivated for 24 h at 37 °C in Nutrient broth (Merck) to assure late exponential phase. Aliquots of $100\,\mu$ l of the suspension were spread plated in duplicate onto previously prepared VRB - Mug plates (Merck) to obtain evenly seeded plates. The glass disks containing different Ag concentrations (5% and 20%) were autoclaved and cooled before carefully placed on the agar plates and incubated for 24 h at 37 °C. Pure glass with no coatings was used as negative control and pristine glass samples before subjected to high temperatures as positive control.

The NLO studies were carried out by a femtosecond Ti: sapphire oscillator system (Chameleon, Coherent) delivering nearly bandwidth limited laser pulses at 800 nm. The oscillator was pumped with a Nd:YVO₄ laser operating at 527 nm. The output pulses from the oscillator were generated at 80 MHz repetition rate and had \approx 140 fs pulse duration. This system was tunable from 680 to 1060 nm. The initial diameter of the laser beam was 2 mm and was focused through a plano-convex lens of f=10 cm. The sample moved along the beam propagation path via the focal point and recorded scanned transmittance data manually at every Z position using the detector (Thermal Sensor,

Field-Max). The estimated beam waist (diameter) was $\approx 25 \,\mu\text{m}$ and the corresponding Rayleigh range (Z_r) of $\approx 2 \,\text{mm}$ which guarantees the validity of thin sample approximation since the sample length was $<<Z_r$. Typically, the peak intensities used for the open and closed apertures were $\approx 0.1 \,\text{GW}\,\text{cm}^{-2}$ and $\approx 0.03 \,\text{GW}\,\text{cm}^{-2}$, respectively. The complete details and schematic of the Z-scan experiments have been explained in our previous works.^[29–31]

3. Results and Discussion

3.1. Structural Studies

Figure 1a shows the XRD patterns of the Ag pristine sample and the sample annealed at various temperature up to 650 °C for 1 h. The XRD of the Ag Pristine sample did not exhibit any diffraction peaks. However, the thermally treated samples showed very sharp intense peaks in the XRD patterns due to the rapid growth and agglomeration of the Ag NCs in the glass



Figure 1. a) XRD patterns of the pristine sample and the Ag exchange sample annealed at various temperatures; b) RBS spectra of pristine and annealed sample at various temperatures upto 650 °C for 1h.



matrix with the crystallographic planes of (111), (200), (220), and (311) and the FCC crystalline structures corresponding to the 38.2° , 44.3° , 64.6° , and 77.2° values (JCPDS file no.00-004-0783).^[19] The intensity of the diffraction peaks of the Ag increased with increasing the annealing temperatures up to 650° C, indicating the rapid diffusion of the Ag atoms and growth of Ag NCs in the glassy matrix at the higher temperatures.

The crystalline size was controlled by the thermal treatment and was calculated for the Ag NCs using the Scherrer equation at the different temperatures. The average crystalline sizes were 4.2 ± 1 , 5.1 ± 1 , 6.2 ± 1 , 7.8 ± 1 , and 8.5 ± 1 nm for the 450– 650 °C thermal treated samples. Thus, with an increase in the annealing temperature an increase in the NCs size was obtained.

RBS was performed to study the distribution of Ag in Ag pristine sample and thermally treated samples in the oxidized atmosphere at different temperatures up to 650 °C as shown in Figure 1b. The Ag peak intensity near the surface in Ag pristine sample was higher than the thermal treated samples indicating that the concentration of Ag⁺ ions were much higher at the glass surface before annealing. However, after the Ag pristine samples were thermally heated at different temperatures up to 650 °C, the Ag peak intensity was found to be systematically reduced with an increase in temperature. This reveals that the Ag atoms were incorporated into the glass matrix during the post thermal treatments. The Ag atoms diffused inside the glass material during annealing process. The Ag atoms also accumulated slightly near the glassy surface (slight increase of Ag near surface) during thermal treatment at the lower temperatures.^[18,19,32] The near surface accumulation was probably be due to the agglomeration of the Ag atoms that diffused inside the glass matrix.^[18]

3.2. Chemical Studies by XPS

XPS was carried out to study the chemical changes taken place after Ag ion-exchange process and post thermal treatment. The XPS results and fits of the Ag as exchanged sample and the sample annealed at 650 °C for 1 h are shown in Figures 2 and 3. The XPS survey spectrum of the pristine sample clearly shows the expected elements such as C, O, C-KVV, O-KLL, Ag, Si, Na, and Ca. A first order quantification approach^[33] indicated that the concentration of Ag on the glassy surface was approximately 2 at%. Normal contamination of C and O on the surface and the species such as Na, Si, Ca could be detected. Figures 2c and 3b show the detail energy region of the O-1s level for the pristine and sample annealed at 650 °C for 1 h. The fits reveal SiO₂, CO₂, H₂O, and OH-groups as indicated.

The C-1s peaks for the pristine sample and 650 °C sample are assigned to C–C, C–OH, C–O–C, C=O and C=O as shown in **Figure 2b** and 3a. Figure 2f and 3e show the Ag 3d spectra for the pristine and 650 °C samples. According to the fit results, the binding energies of the Ag 3d_{5/2} peak in the pristine sample were at 367.4 eV for Ag(II)/AgO, 368.0 eV for Ag(I) + Ag(III), 368.4 eV for Ag(I), and 369.2 eV for the Ag(III) satellite peak [see section in ESM 2 of the supplementary materials (SM)], which compared very well with literature.^[34] After annealing, the calculated ratio of the Ag (I)/(Ag (0) +Ag (I)) decreased from 1 to 0.08. These results confirmed that Ag⁺ ionic atoms were reduced

to Ag neutral atoms under thermal treatment. If one compares the Ag 3d peak areas of the annealed sample (650 °C) with that of the pristine sample, the concentration of Ag was less than 2 at%. The fits give a clear indication that the peak at approximately 368 eV contained mostly Ag (0) and very small amounts of Ag (I), seen in section ESM 1 of the supplementary materials (SM). In the pristine sample the ratio Ag (I)/(Ag (0) +Ag (I)) is 1.00 indicating mainly Ag (I), AgO on the surface and in the 650 °C sample this ratio is 0.17. For the pristine sample there was a clear indication of AgO on the surface. The result revealed that the ratio Ag (I)/(Ag (0) +Ag (I)) of the pristine sample was higher than that of the annealed sample (650 °C).

But it was reported that the AgO is unstable at higher thermal treatment and it dissociates into pure metal at higher temperatures.^[18,35] The ratio of the Ag (I)/(Ag (0) +Ag (I)) reduced to 0.17 in the annealed sample (650 °C), due to the reduction of AgO and the formation of pure metallic nanoclusters. The concentration of the Ag was approximately 2 at% and the indepth distribution was uniformly, with an island type with a glass overlayer according to the shape of the background to higher binding energies.^[36,37]

In summary the XPS results revealed that the Ag was present in the form of Ag oxide (AgO) in the pristine sample and in the metallic form (Ag⁰) for the annealed sample at 650 °C with the desegregation of the Ag atoms into the bulk.

3.3. Tuning of Plasmonic Behavior of Ag NCs Diffused in Glass Matrix

Figure 4a shows the optical absorption spectrum of the Ag pristine sample and thermally annealed samples. The optical spectrum of the Ag pristine sample did not indicate any plasmonic peaks in the spectrum indicating that the Ag existed mainly in the form of Ag⁺ ions and Ag NCs in the glass matrix as also confirmed from XPS study. Ag atom aggregation did not occur or the size of the Ag clusters was less than 1 nm during the ion exchange process.^[18,19,21] The glass matrix generally act as a host material which provides sufficient electrons to reduce the population of the Ag⁺ ions into neutral Ag⁰ atoms. During post thermal treatment, the electrons are captured from the glass impurities which are further used to reduce more Ag⁺ ions into the population of Ag⁰ neutral atoms. The sample annealed at 450 °C for 1h displayed an evident plasmon peak at about 433 nm, which is attributed due the localized surface plasmon resonance (SPR) band of the Ag NCs in the glass matrix.

The thermal treatment induced rapid growth and agglomeration of the Ag atoms inside the glass matrix. The plasmonic peaks were located at around 433, 428, 426, 422, and 418 nm for the sample annealed at the different temperatures from 450 to 650 °C for 1 h, respectively. A blue shift of 15 nm was observed during the post thermal treatment upto 650 °C for 1 h. As the thermal annealing temperature increased, the plasmonic spectra of the Ag NCs in the glass matrix became more and more obvious and the plasmonic peak width has gradually narrowed. The intensity of the absorption peak increased significantly and the width of the absorption peak reduced systemically with the increase of thermal treatment indicates an increase of the volume fraction of Ag atoms in the glass matrix. Because more







Figure 2. XPS spectra of the Ag pristine sample: a) survey scan; b) C 1s; c) O 1s; d) Si 2p; e) Na 1s, and f) Ag 3d energy regions.

population of Ag⁺ ions converted into more Ag⁰ neutral atoms with increasing thermal treatment, which indicated towards the rapid growth and agglomeration of the Ag NCs in the glass matrix.^[18,19,38–40] Due to the mean free path effect of the electrons for a small clusters ($R \le 10$ nm),^[18] a significant decrease in FWHM was observed with increasing the clusters size during post thermal treatment as shown in Figure 4b.

Consider the free particle behavior of electrons, the average size of the Ag nanoclusters was obtained using the following equation

$$R = v_F \frac{\hbar}{\Delta E}$$

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Figure 3. XPS spectra of the Ag (650 °C) sample: a) C 1s; b) O 1s; c) Si 2p; d) Na 1s, and e) Ag 3d regions.

Or,
$$d = 2R = 2\frac{\hbar v_F}{\Delta E}$$
 (1)

where, *d* is the average size of the Ag nanoclusters, $v_f = 1.39 * 10^6 \text{ m s}^{-1}$ is the Fermi velocity for the bulk Ag, where \hbar is Planck's constant and ΔE (in eV units) in Equation (1) is the band width at full- width at half maximum (FWHM) of the absorption band, Figure 4a. Equation (1) is only valid if the clusters ($R \le 10 \text{ nm}$) size is much smaller than that of the mean free path of the electrons in the bulk Ag. At room temperature, the mean

free path of the electrons is around 27 nm for bulk Ag.^[8–9] The average size of the Ag NCs were calculated as 2.1, 2.3, 2.5, 3.7, and 3.9 nm after annealing in the oxidized atmosphere at the different temperatures ranging from 450 to 650 °C for 1 h. The results revealed that the size of the Ag NCs increased with increasing the thermal treatment temperature due to the rapid diffusion and aggregation of the Ag atoms in the glass matrix.^[8]

The particle size and microstructures of the thermally treated samples at different temperatures were also observed by FEGTEM studies. Figure 5–8 show the FEGTEM images for **ADVANCED** SCIENCE NEWS _



Figure 4. a) Optical absorption spectra of the Ag nanocomposites glass obtained at different temperatures; b) FWHM and particle size versus annealing temperature.

the Ag as exchanged sample annealed at various temperatures as indicated.

It can be seen from each FEGTEM images that a large number of black clusters were obtained due to the Ag diffusion in the glass matrix with a regular spherical shape with a particle size distribution between 2 and 4 nm. The crystal structures of the Ag NCs in the glass matrix were characterized by SAED and the high resolution transmission electron microscope (HRTEM). The average size of the Ag NCs estimated from the TEM micrographs were calculated as 2.1 ± 0.5 , 2.7 ± 0.5 , 2.9 ± 0.5 , 3.5 ± 0.5 , and 3.9 ± 0.5 nm, respectively for the Ag pristine sample thermally treated at different temperatures from 450 to 650 °C, respectively for 1 h (as shown in the histogram plot) which closely matched with the cluster size calculated by Equation (1).

The high resolution TEM images for the sample annealed at 550, 600, and 650 °C show that the spherical particles consisted of a crystal lattice with a d-spacing of 0.24 nm, which corresponds to the (111) plane of Ag as shown in Figures 6–8. The SAED patterns were also obtained for the sample annealed at 600 and 650 °C, which indicated the presence of the crystallographic plane (111) of the Ag⁰ clusters as shown in



Figures 7 and 8. These results also closely matched with results obtained from the UV-Visible absorption studies.

It must be pointed out that the calculated clusters sizes obtained from FEGTEM are smaller than the crystallite size as calculated from using the Scherrer formula and the XRD patterns. Inwati et al.^[41] have recently reported a similar trend of crystalline size difference as estimated from XRD which was also not consistent with the size estimated from FEGTEM. This may be attributed to the effect of crystal breakage due to crushing of the silver embedded glass into the fine powder, which has been used for the FEGTEM measurements. The Scherrer equation is also just giving an estimation of the crystalline size and can be influenced by several other factors such as the instrumental factors and macrostrain in the lattice.

3.4. Tuning of Photoluminescence Behavior of Ag NCs Diffused in Glass Matrix

Figures 9-11 show the PL spectra excited by three different wavelengths of 325, 375, and 450 nm, respectively for the Ag ion exchanged sample and annealed samples. The PL in Figure 9a-f for an excitation wavelength of 325 nm could be best fitted into five peaks whose peak positions varied in the different samples as the annealing temperatures were varied. These appeared at 380, 443, 480, 534, and 584 nm, respectively for the pristine sample. The different peak positions for these emissions are shown in the electronic supplementary material [ESM-2]. Similarly the PL emission from the 375 nm excitation, Figure 10b-d, for pristine, annealed at 500 and 550°C, respectively could be best fitted into two peaks. The inset in Figure 11 shows that the broad PL peak (obtained at 450 nm) was present only in the pristine sample which could be best fitted into three peaks at 490, 535, and 581 nm, respectively. These emissions in the different samples were mainly originated from the four different regions due the presence of several ionic states of the Ag ions, naturally present defects and newly generated imperfections inside the glass matrix during the ion exchange processes. The possible PL band diagram for these samples has been proposed in Figure 12. The PL emission observed in the region 363–413 nm can be attributed to the presence of Ag⁺ ions in distorted octahedral sites in the glass matrix.^[42]

The emissions in the range of 438-480 nm are assigned to the presence of Ag₂⁺ sites, Ag dimmers and Ag⁺ - Ag⁰ pairs whereas the region from 490 to 550 nm can be attributed to the presence of Ag₃⁺ sites and partly Ag dimmers inside the glass matrix.^[42–45] In addition to these a PL band in the region 581-590 may be associated with L-centers, Si-O based defects or non-bridging oxygen centers inside the glass matrix.^[42] Beside this the electron from the highest energy levels can be nonradiatively transferred to the lower unoccupied energy states for different emissions. The differences on the PL maxima peaks position may be due to the existence of different site symmetries for each glassy matrix. The step 1 in the figure shows the excitation process of electrons by 325, 375, and 450 nm from Ag⁺ free ions in the ground states to the Ag $4d^9$ 5s states of silver in the glass matrix. The step 2, step 3 and step 4 the different emission band observed due the presence of different ionic states of silver ions and presence of crystal defects, respectively. The near-surface accumulation in the pristine sample has been







Figure 5. FEGTEM image of Ag ion exchanged glass after annealing at various temperatures: a) at 450 $^{\circ}$ C and b) particle size distribution curve; c) at 500 $^{\circ}$ C and d) particle size distribution curve.

ascribed to the presence of Ag_2^+ ions and Ag_3^+ ions coming from the bath used, which subsequently converts into Ag neutral atoms after annealing as evident form the PL spectra at higher annealing temperatures.^[43] The different peak positions for the PL emissions excited by three wavelengths of 325, 375, and 450 nm, respectively as shown in the electronic supplementary material [ESM-2].

3.5. Tuning of NLO Behavior of Ag NCs Diffused in Glass Matrix

The third order NLO properties of the Ag NCs incorporated into the glass matrix by a thermal ion exchange process and annealed at various temperatures have been studied using the Z-scan technique. The coefficients of nonlinear absorption, nonlinear refraction, third-order nonlinear susceptibility have been obtained. **Figure 13** demonstrates the open aperture Z-scan data of the Ag NCs incorporated into the glass annealed at various temperatures (a) 550°C, (b) 600°C, (c) 650°C, and (d) without thermal treatment, recorded at a peak intensity of $0.1 \,\mathrm{GW}\,\mathrm{cm}^{-2}$. It is evident that the appearance of the curves in all cases represents RSA except in the case of a sample (Figure 13d) without annealing. The data was analyzed by using the standard transmittance equation with two photon absorption coefficient (β) and the evaluated (β) values are 6.2 × 10⁻⁸, 8.8 × 10⁻⁸, and $2.9 \times 10^{-8}\,\text{cm}\,\text{W}^{-1}$ for Ag nanoclusters incorporated into the glass matrix annealed at various temperatures of 550 °C, 600 °C, and 650 °C, respectively. The two photon absorption coefficient (β) of the Ag nanoclusters incorporated into the glass matrix annealed at 600 °C shows the highest absorption coefficient while the sample annealed at 650 °C shows a decrease value of the two photon absorption coefficient (β). This is due to the optical limiting threshold conditions that got reduced after thermal treatment at the high temperature as the Ag nanoclusters became larger.^[46,47] The reason behind the presence of two photon absorption in these samples with the excitation at







Figure 6. FEGTEM image of Ag ion exchanged glass sample: a) at 550 °C and b) particle size distribution curve; c) HRTEM image of Ag doped glass sample at 550 °C.

800 nm could be based on the intra band (s-p) transitions (or) free carrier absorption since the absorption band (\approx 420 nm) of the samples is nearer to the SPR band of Ag nanoparticles. On the other hand excitation with 800 nm and at the same peak intensity illustrated no nonlinear absorption in Ag nanoclusters dispersed in soda lime glass without annealing. This behavior could be due to the absence of the SPR band in this case because no spherical Ag nanoparticles were embedded into the glass matrix. Similarly, Figure 14 illustrates closed aperture data of Ag nanoclusters embedded in soda lime glass matrix at different temperatures (a) 550 °C, (b) 600 °C, (c) 650 °C, and (d) without annealing, recorded at a peak intensity of $0.03 \,\mathrm{GW \, cm^{-2}}$. Regarding this nonlinear response, data depicted a peak-valley signature due to self-focusing (or) self-defocussing. It was observed that samples at 550°C (Figure 14a) and at 650°C (Figure 14c) exhibited positive nonlinearity and, the sample at 600 °C (Figure 14b) showed negative nonlinearity which could be due to free carrier absorption. The nonlinear refraction coefficient n₂ values were deduced by fitting the closed aperture curves using the standard equation and the n2 values obtained were 2×10^{-12} , 6×10^{-12} , and $0.8 \times 10^{-12} \text{ cm}^2 \text{W}^{-1}$ for the samples annealed at the different temperatures of 550, 600, and 650 °C, respectively. It is clearly observed from the results that the annealing temperature influenced the electronic configura-tion of the system.^[48,49] The annealed samples demonstrated large third order nonlinearities even at low excitation intensities. One of the possible reasons for large nonlinearities could due to

the influence of thermal nonlinearity along with electronic nonlinearity since more number of pulses (80 MHz) per second were interacting with the sample at the same place which possibly resulted in heating the sample. The possibility of an error to occur in the experiment as well as analysis was estimated to be 5-10%. This error could be because of fluctuation in laser power, estimation of input peak intensities s and theoretical fitting procedures etc.

3.6. Thermodynamic Modeling for the Nucleation and Growth of Ag NCs in Glass Matrix

The system followed the $Ag^+ \rightarrow Ag^0$ route during the thermal treatment process where adequate electrons were supplied by the host material in order to reduce more Ag^+ into a higher population of Ag^0 atoms.

The transformation of the Ag⁺ ions to Ag⁰ neutral atoms under thermal treatments, are explained below where the glass impurities provides the necessary electrons to reduce the Ag⁺ \rightarrow Ag⁰ (Scheme 1).^[41]

In such metallic reduction, ionic species need enough energy to cross the barrier potential for breaking the Ag—O bond in the glassy matrix. The energy required for breaking the Ag—O bonds can be considered as the activation energy (E_a) in the thermal process to form Si—O and Ag—Ag bonds. In the present study, we have thoroughly studied the thermodynamic parameters







Figure 7. FEGTEM image of Ag ion exchanged glass sample: a) at 600 °C and b) particle size distribution curve; c) HRTEM image of Ag doped glass sample at 600 °C; d) SAED pattern.

such as the activation energy, enthalpy (Δ H), entropy (Δ S), and Gibbs free energy (Δ G) for the pristine and thermally treated samples at the different temperatures (see section in supplementary materials (SM-3).

The Ag ion-exchange process at 390 °C lead to the diffusion of Ag⁺ ions in the glassy matrix after replacing the Na⁺ atoms of the glass matrix and the Ag neutral atoms have diffused towards the glassy surface after annealing at the different temperatures. As a result, the surface accumulated Ag atoms showed a significant change in the optical behavior due to the absorption and scattering phenomenon when it interacts with the light.^[41] The higher dispersion of Ag atoms at the glassy surface affects the optical response. Thus, the Ag⁰ absorbance data was used to calculate the activation energy and also other thermodynamic parameters The UV-Vis absorbance spectra was recorded to study the changes in the optical behavior using the Lambert Beer's Law according to the following relation:

$$A_{\rm abs} = a \times b \times C \tag{2}$$

where A_{abs} is absorbance, *a* is the molar absorptivity, *b* is the path length of the light through the sample, and *C* is the concentration of the sample.

The activation energy was obtained using an Arrhenius equation^[43-44] with respect to annealing temperatures, which was fitted as-

$$A_{abs} = Ae^{-E_a/2.303RT}$$
(3)

The modified equation given as

$$\ln(A_{\rm abs}) = \ln(A) - \frac{E_a}{2.303RT} \tag{4}$$

where, abs = absorbance for Ag NCs, T = applied temperature (Kelvin), R = Gas constant (8.314 J (mol K)⁻¹, A = frequency factor, $E_a =$ activation energy (J mol⁻¹).

The relation between absorbance and the annealed temperature was investigated using the Arrhenius equation where the straight line plot abtaine with a $(-E_a/R)$ slope as shown in **Figure 15**a. The graph show a 1st order growth mechanism for the Ag NCs formation. The diffusion rate of the Ag for the nanocluster formation is related to the activation energy required for breaking the bonds. Hence, the optical density or absorbance of the optical spectra was used an authentic experimental data for the calculation of activation energy (E_a) in this process.

The E_a value was use to calculate the enthalpy^[50] (ΔH) of the system in the following equation

$$\Delta H = E_a - 2.303RT \tag{5}$$







Figure 8. FEGTEM image of Ag ion exchanged glass sample: a) at 650 °C and b) particle size distribution curve; c) HRTEM image of Ag doped glass sample at 650 °C; d) SAED pattern.

The enthalpy of the thermal process gives the information for the kinetic rate of the Ag nanoclustering under the thermal conditions. The Ag⁰ growth follows the endothermic as well as exothermic process and the enthalpy values are shown in the electronic supplementary material (ESM-3) for all the thermal treated samples. The system show an endothermic process with 41.33–45.15 kJ mol⁻¹ as the temperatures increased from 450 to 650 °C. It is clearly shown that the process became more endothermic with increasing the annealing temperature as the enthalpy values increased.

The enthalpy values infer the reduction of ionic Ag to neutral atoms and their arrangement at different crystalline plane like (111), (200), (220), and (311) as shown in Figure 1a. In the crystalline arrangements of the Ag atoms, the kinetic rate increases the FCC array for the crystal lattice inside the matrix.^[51,52]

Furthermore, the Gibbs energy (ΔG) and entropy (ΔS) values are investigated at different temperature which are given as follow-

The Gibbs Free energy is given by

 $\Delta G = -2.303 RT \ln(A_{\rm abs}) \tag{6}$

Also we know that

$$\Delta G = \Delta H - T \Delta S \tag{7}$$

For Ag clustering the Gibbs energy (ΔG) and entropy (ΔS) were obtained using Equations (5) and (6) in Equation (7) given as-

$$-2.303 RT \ln(A_{abc}) = E_a - 2.303 RT - T\Delta S$$

$$-2.303 RT \ln\left(Ae^{\frac{-E_a}{RT}}\right) = E_a - 2.303 RT - T\Delta S$$

Entropy(
$$\Delta S$$
) = $\frac{[E_a - 2.303 RT + 2.303 RT \ln(abc)]}{T}$ (8)

Equation was modified as under-

$$\Delta S = \left[\frac{E_a}{T}\right] - 2.303R[1 - \ln(abs)]$$







Figure 9. a) PL spectra of the Ag ion-exchanged pristine glass and after annealing at various temperatures at excitation wavelength of 325 nm; and the fits of the spectra for b) pristine; c) annealed at 500 °C; d) annealed at 550 °C as well as enlarge spectra obtained after annealed e) at 600 °C; and f) at 650 °C, respectively.

Entropy(
$$\Delta S$$
) = $\frac{(E_a - 2.303 RT + 2.303 RT \log(abs))}{T}$ (9)

the ΔG calculation-

 $\Delta G = -2.303 \, RT \log(abs) \tag{10}$

Because the optical absorbance reveals the $Ag^+\!\to\!Ag^0$ confirmation that's why the absorbance used as a variable for

Where, all the symbols are usual in the equation at applied temperatures for the required activation energy and Gibbs energy







Figure 10. a) PL spectra of Ag ion-exchanged pristine glass and after annealing at various temperatures at excitation wavelength of 375 nm; and the fits of the spectra for (b) pristine; (c) annealed at 500 °C; d) annealed at 550 °C as well as enlarge spectra obtained after annealed (e) at 600 °C; and (f) at 650 °C, respectively.

both. It is clearly indicated that the entropy increased from 450 to 650 °C in order to define the higher disorder arrangement of the Ag atoms in the thermal process. The applied higher temperature supports the accumulations of the Ag atoms with positive changes in the entropic values. Additionally, both ΔH and ΔS show an inverse trend as enthalpy-entropy compensation mutual relationship which optimized the minimum energy of the thermal system.

A mutual relationship among the ΔG , ΔH , and ΔS has developed for the Ag NCs growth under the thermal process as shown in Figure 15b. In the graph, it is clearly shown that ΔS and ΔG both have a reverse trend with respect to ΔH values. The Ag⁺ ions replaced the Na⁺ ions in the glass host materials during the ion exchange process and bound to the non-bridging oxygen atoms in the dielectric glass host materials. The Ag–O bonds







Figure 11. PL spectra of Ag ion-exchanged pristine glass and after annealing at various temperatures for an excitation wavelength of 450 nm. The inset shows the fits for the pristine sample.

were ruptured during post thermal treatment under the oxidized atmosphere to form Si—O and Ag—Ag bonds respectively. Thus, ΔH and ΔS values increased due to the adequate thermal energy involved in bond rupturing and diffused different Ag atoms in the glass host materials. So, the ΔH , ΔS , and ΔG mutually explain the orientations and distribution of Ag NCs in the glass matrix

It is well known that the spontaneity of any process can be represented by the Gibbs energy.^[41,50–53] In our case, the ΔG increase with increasing the annealed temperatures may be due

to the atomic arrangement of Ag in the glass matrix. This is considered that at higher temperature the process becomes more spontaneous with higher thermal energy as the Ag atoms precipitate towards the surface and forming NCs. Moreover, the process is less spontaneous at lower temperature because the reduction of Ag ions only completed at the lower temperature. This mutual relevance supports to the Ag ion-exchange and diffusion of the Ag atoms at lower to higher temperatures, respectively. The ΔG , ΔH , and ΔS values are interdependent with each other to utilize the heat during the growth and clustering of the Ag NCs under thermal reaction. Such, thermodynamic synergy helps to know the atomic distribution or dispersion mechanism of Ag under the annealing condition.

In the present work, the Ag atoms were incorporated into the glass matrix during post thermal treatment under oxidized atmosphere and an Arrhenius plot was obtained with the help of using UV-Visible absorbance as an authentic data at various temperatures and the estimated thermal activation energy was found to be 59 kJ mol⁻¹. The other thermodynamic aspects such as ΔG , ΔH , and ΔS were also obtained using thermal activation energy during post annealing process in oxidized atmosphere. Hence, the thermodynamic models reveals the kinetics growth mechanism of Ag NCs diffused in the glass host materials during the thermal process and the results are approximately similar related to UV-visible absorbance based studies.

3.7. Antibacterial Activity of Ag NCs Embedded Glass Matrix

It is well known that the different metals such as Ag, Cu, Ni, and Au etc. show different antibacterial activities against the gram



Figure 12. PL energy level diagram of Ag ion-exchanged glass after annealing at various temperatures.







Figure 13. Open aperture Z-scan data of Ag nanoclusters embedded in soda lime glass annealed at different temperatures (a) 550, (b) 600, (c) 650, and (d) sample without annealing recorded with peak intensity of \approx 0.1 GW cm⁻² at a 800 nm wavelength using \approx 150 fs pulses. Open circles represent the experimental data while solid lines are theoretical fits.



Figure 14. Closed aperture Z-scan data of Ag nanoclusters embedded in the soda lime glass annealed at different temperatures (a) 550, (b) 600, (c) 650, and (d) sample without annealing recorded with peak intensity of \approx 0.03 GW cm⁻² at a 800 nm wavelength using \approx 150 fs pulses. Open circles represent the experimental data while solid lines are theoretical fits.



Scheme 1. Transformation of the Ag^+ ions into the Ag^0 neutral atoms in the glass matrix.

negative species *E. coli*. Because each metal has a different atomic sensitivity factor responsible for the inhibition of cell growth. The present study however, was not focused on the comparison of effects of different metals on the antimicrobial activities, but instead only focused on the changes of antimicrobial activity of Ag treated at different temperatures against the gram negative species *E. coli* and which showed resistance against the different bacteria.^[54,55]

The antibacterial effect of Ag NCs incorporated into the glass as host material was monitored by the disk diffusion assay against the gram negative species E. coli. The antibacterial studies of Ag doped glass sample was studied on the basis of the concentration effect. It is well known that the Ag⁺ concentration on the glassy surface is higher in the case of the Ag asexchanged sample.^[18,19] It means most of the Ag⁺ ions only exist on the glass surface during ion exchange. The Ag concentration on the glassy surface reduced with respect to the post thermal treatment i.e. 450-650 °C which means the Ag atoms were incorporated into the bulk glass after thermal treatment. Thus we can say that the Ag⁺ concentration on the glassy surface in the case of the Ag as-exchanged sample was higher than that of the post thermal treatment condition samples which is well supported by the RBS based results. In our earlier studies,^[18] no Raman band was observed for the Ag ion exchanged glass samples annealed at the different temperatures which gave a clear indication that the silver NCs were embedded in the glass matrix as metallic silver clusters and not respond to Raman spectroscopy. Simo et al, reported the SERS studies of Ag ion exchange samples after removing the glass layer on the surface of the Ag NCs.^[56] Our results focused only on the surface concentration of Ag⁺ against antimicrobial activities. Because the antibacterial efficiency of Ag⁺ ions were found more effective as compare to the Ag neutral atoms. Prakash et al.^[57] found that the engineering of shapes and sizes causes significant variations in



the physical and electrical properties adding flavor to the tunability and flexibility in multifunctional applications of the resulting nanocomposites. This not only enhances the photocatalytic and antibacterial activities but also extends its utilization in broad field of energy and environmental applications. As depicted in Figure 16, the inhibition zones around the glass samples were reduced by increased annealing temperatures. Zones were clear and larger at 450 °C and remained visible at temperatures of 550-600°C but were not detected at 650 °C. Limited differences in antibacterial activity were observed by using either 3 or 10% Ag (results not shown). Both concentrations showed decreasing activity at temperatures of 650 °C. It is well known that a higher population of Ag ions interact with the cell membrane and some of the Ag ions also incorporated into the cells causing the death of the cell as shown in Figure 16. Therefore it can be clearly seen that the inhibition of bacterial growth was found to be more substantial than samples annealed at 600°C because of enhanced Ag⁺ ions present in the glass matrix. The



Figure 15. a) The Arrhenius plot for the activation energy calculation at different temperatures; b) Mutual relationship for enthalpy, entropy and Gibbs energy for the thermal growth mechanism of Ag nanoclusters in the glass matrix.





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Figure 16. a) Schematic diagram depicting microbiological evolution of Ag NCs in an annealed ion exchanged soda- lime glass.

reduced antibacterial activity at higher annealing temperatures was consistent with the reduced Ag concentrations on the surface of the glass due to the increased diffusion of the metal nanoclusters inside the glass at higher temperatures. With the interaction of releasing Ag^+ to the bacterial cells, there could be two possible explanations.

One is that the Ag⁺ entered into the cell wall and attacked the cell organelles which disturbed the cell metabolism and eventually the cell died due to the inhibition or disturbance of cell metabolic processes as shown in Figure 16. The other might be that the cell line got ruptured causing the plasma fluid to come out of the cell, including cell organelles, and the cell died due to the leakage. During the Ag ion-exchanged (Na⁺–Ag⁺) more Ag⁺ ions were obtained in the glass matrix and these ions are luminescent in nature, which were formed during thermal treatment below the threshold temperature. But when the annealing temperature increased from 450 to $650 \,^{\circ}$ C, the large population of the Ag⁺ ions reduced to Ag⁰ neutral atoms. Thus the inhibition of cell growth increased more up to the threshold temperatures. Durucan and Akkopru^[35] reported that the Ag ion exchange process at temperatures higher than 300 °C induces an ionic exchange process between the molten salt bath of AgNO3 and NaNO3 in the glass substrate, thus reducing the availability of Ag⁺ ions on the glass surface and similar antibacterial results were obtained, as discussed previously. Kumar et al.^[58] found that undoped ZnO nanoparticles showed strong antibacterial activity, while ZnO:Ag nanoparticles did not show any antibacterial behavior attributed to the decrease in defects on the surface of the ZnO nanoparticles.

4. Conclusions

The Ag ions were diffused successfully in a glass matrix to form NCs by a simple ion-exchange followed by thermal treatment in an oxidized atmosphere at different temperatures. The XRD results revealed the FCC crystalline structures of the Ag NCs after thermal treatment. HRTEM images confirmed the spherical Ag NCs (d₁₁₁ = 0.24 nm) with a maximum cluster size of 3.9 nm at 650 °C which agreed with the clusters size calculated by UV-visible absorption based results. The UV-vis, PL, XPS, TEM and RBS analysis confirmed the rapid cluster growth and agglomeration of the Ag atoms with an increasing annealing temperature. A blue shift of 15 nm of the localized SPR peak was found due to the post thermal treatment process. The thermodynamic behavior of the Ag NCs were studied for the thermal process where an activation energy of $59 \text{ kJ} \text{ mol}^{-1}$ was calculated. The thermodynamic aspects such as entropy, enthalpy and Gibbs energy were calculated by considering the UV-Visible absorbance results to confirm the mechanism for the rapid growth and agglomeration of the Ag NCs and a model was proposed. The thermal treated samples demonstrated large third order nonlinearities even at low excitation intensities. The large non-

linearities could be due to the influence of thermal nonlinearity along with electronic nonlinearity since a higher number of pulses (80 MHz) per second were interacting with the sample at the same place which possibly resulted in heating of the sample. These properties are more suitable for the various applications in optical data storage, optical limiting and object's contrast enhancement. A reduced antibacterial activity at higher annealing temperatures was consistent with the reduced Ag concentrations on the surface of the glass due to an increase diffusion of Ag at higher temperatures.

Supporting Information

Supporting information is available from the Wiley Online Library or from the author.

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Conflicts of Interest

The authors declare no conflict of interest.

Keywords

ion exchange, RBS, surface plasmon resonance, XPS, Z scan technique

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