Structural and plasmonic studies of Ag nanoparticles in silica glass hosts

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Silica glassy materials doped with Ag were prepared through sol gel route. The structural studies of the prepared samples showed an icosahedral morphology of the nanocrystals formed along with spherical morphology. The XRD and TEM data confirmed the formation of silver nanoparticles of size between 20 and 22nm. The surface plasmon resonance (SPR) of silver nanoparticles with spherical morphology was studied with the discrete dipole approximation. The shape and size effects of the nanoparticles can induce distinctive features of the SPR spectrum. It has been shown that such effects can induce peak intensity enhancement, wavelength shift and spectral broadening of the SPR spectra of the nanoparticles. The results obtained depend on the existence of highly localized plasmonic oscillations. An attempt has also been made to calculate the van der Waals force between nanoparticles.

INTRODUCTION

Nearly spherical metal particles of nanometer dimensions embedded in silicate glass can be fabricated by several means. Their structural and optical properties, promising for potential applications, depend on concentration, size, shape, spatial arrangement and configuration of the nanoparticles [1, 2]. Plasmonic properties of silver nanoparticles (AgNPs) have been extensively 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 [3]. In the past years, a number of applications based on the SPR of AgNPs have been presented, in particular for biosensing, surface-enhanced Raman scattering, and plasmon circuitry [4]. Several of these applications take advantage of the engineering of AgNPs plasmonic response that depends on their size, shape, dielectric environment, and on mutual electromagnetic interactions among particles in close proximity [5]. In this work we doped silver nanoparticles into silica glasses via sol-gel route. Here the prime objective is to study the structural features of the prepared samples. We also used a DDA code for studying the influence of shape, size and dielectric environment on the SPR of AgNPs. The results reveal that the shape and the size of AgNPs strongly affect the SPR.

EXPERIMENTAL

Sample with 0.02% and 0.04 % silver in silica glasses were prepared through the sol-gel route. The tetraethylorthosilicate (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. The samples where characterized using XRD, TEM and spectrophotometer.
RESULTS AND DISCUSSIONS

Structural studies

The assignments of the peaks were done and the planes [111], [200], [220] and [311] were identified with the JCDPS card number 04-0783. The average size of the crystallites was found to be in the range 20-22 nm. Fig. 1 shows the TEM images obtained for sample. The inset of the images shows the electron diffraction pattern and the crystallite size distribution of the respective samples. The growth of particle size of silver in silica matrix depends mainly on the diffusion coefficient and activation energy of coalescence and more specifically on the heat treatment time and temperature of the matrix [6]. Thus it is quite evident that spherical as well as icosahedral morphology is observed for samples [7].

Surface plasmon studies

In the case of noble metal spherical nanoparticles, the extinction cross-section $\sigma_{\text{EXT}}$ in the visible range can be accurately calculated by analytical expressions [8]. The most applied expression was developed by Draine and Goodman and this was used in the present work. We adopted a size-corrected dielectric constant, the simplest choice for our calculations. Assuming that $r$ to be equal to the effective radius of the particle, we have

$$r = (3V/4\pi)^{1/3} \rightarrow (1)$$

where $V$ is particle volume, independent of particle shape. In the visible wavelengths, AgNPs have more intense and sharp plasmonic resonance. This may be due to the different dielectric properties originated by the small overlap between the SPR and the interband transitions in Ag that start at 320 nm [8]. The choice of silver nanostructures allows the highest sensitivity for studying the effect of shape and size on the SPR. Fig. 2 shows the experimental and calculated the SPR spectrum for the 20 nm AgNPs. An analysis of the different spectra suggests intensity enhancement, wavelength shift and broadening of the spectrum.

We have also extended our studies to estimate the van der Waals energy between two spherical nanoparticles. The van der Waals interaction between two equal nanospheres is more complicated. In this case we have to take into account the zero-point energies of all modes, including symmetric M and T modes and antisymmetric L modes. The total energy is given by the following expressions with the parameters having the usual meaning [9]
Our approach considers the case of unequal spherical nanoparticles of radii \( R_1, R_2 \). Here, we restrict ourselves to the case of closely spaced nanospheres. Again, the main contribution to the van der Waals forces is due to the modes with large \( m \), and thus contributions from symmetric M modes and antisymmetric L modes can be estimated as

\[
U_{vdW} = U_{vdW}^M + U_{vdW}^L + U_{vdW}^T \rightarrow (2)
\]

where \( \omega_{pl,1} \) and \( \omega_{pl,2} \) are the bulk plasmon frequencies of the spheres and the functions \( f_M \) and \( f_L \) and their sum are shown in fig.3. From this picture, one can see monotonic variation of van der Waals force when \( \omega_{pl,1} \) changes from 0 to \( \infty \) with \( \omega_{pl,2} \) fixed. It is very interesting that contributions of L and M modes do not have monotonic character. If M modes do not exist, the van der Walls forces will be formed by L modes only and have maximum for \( \omega_{pl,1} = \omega_{pl,2} \). Thus, L and M modes give the main contribution to the van der Waals forces[9].

CONCLUSION

The formation of silver nanocrystals was confirmed by XRD and TEM. The TEM images confirm the crystallite size values obtained from XRD. The shape and size effects of the nanoparticles can induce distinctive features of the SPR spectrum. The energy of the van der Waals interaction between two closely placed metallic nanospheres can be taken as the energy of vacuum fluctuations of all plasmonic modes existing in the system. The results obtained depend crucially on the existence of highly localized plasmonic oscillations.

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