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Synthesis and optical characterization of Ag^0 nanoparticles

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ABSTRACT

The results of chemical synthesis and optical behavior of silver nanoparticles with sizes ranging from 2–10 nm which were obtained by reduction of Ag^+ are reported. The material morphology was examined by transmission electron microscopy (TEM) and physical properties were studied by photoluminescence in the range of 400–550 nm using two different excitation wavelengths (320 and 380 nm). The signature provided by the silver plasmon is readily noticed in the silver nanoparticles. The nonlinear optical properties were obtained using a Z-scan setup and agree with previous results obtained by other methods and preparation of samples. In particular, a positive nonlinear refractive index of $5.0115 \times 10^{-10}\,m^2/W$ was obtained for a broad sample of silver nanoparticles between 2 and 10 nm. The agreement between the properties of the thin film sample and the nanoparticles give emphasis to the Z-scan technique for nonlinearity measurements of much more complex metal–dielectric structures.

1. Introduction

The same basic principles of electromagnetic (EM) transmission and reflection, on dielectric and metals, support two different approaches on photonic crystals (PC) and photonics band gaps (PBG). Each one of them exhibit distinctive characteristics, while the dielectric photonic crystals (DPC) are characterized by the typical stopgap [1], the best well-known feature of metal photonic crystals (MPC) is the peaked transmission structure [2], exhaustively studied by Yablonovich et al. on an 1D array of thin metallic films with a thickness of tens of nanometers. Both of them require specific scales because of the particular characteristics of their materials, in the case of DPCs the scale is on the order of wavelengths while for an MPC it is on the order of nanometers. On their own these metal–dielectric structures have already found important applications [3].

The search of new materials in order to build novel devices is now focusing on the fact that the properties of each nanomaterial can be modulated not only through the nature of their constituting units, but also through the distance between particles or the whole system architecture. Core-shell colloidal particles have recently attracted a lot of attention because of the ability to fine-tune their properties. Colloids are ideal building blocks for the creation of PC, because of their ability to self-organize in three-dimensional periodic structures with different symmetries. On the other hand, metallic nanoparticles are well-known nonlinear materials. Therefore, metallic nanoparticles in a dielectric host are highly attractive to build up nonlinear PC devices. In this work we report the synthesis and characterization of Ag^0 nanoparticles and sub-microspheres of SiO_2 embedded with Ag^0, as well as their nonlinear optical features in a thin film.

2. Experiment

Single dispersed colloidal SiO_2 particles were prepared by the well-known Stöber method [4] which consists in the base-catalyzed hydrolysis of tetraetoxilsilano. Aqueous ammonia (11.9 ml of NH_3 at 29%) and 88.1 ml of ethanol were both mixed in an Erlenmeyer flash. This solution was stirred in a water bath at 20 °C, and followed by the addition of 3.6 ml of tetraetoxilsilano under vigorous stirring. The stirring rate was reduced and was kept at a slow rate for 15 h. The solvent was then removed by centrifugation at 3000 rpm for 30 min. This preparation resulted in particles with a diameter between 200 and 400 nm.

Silver sols were prepared using 0.1 g of $AgNO_3$, 100 ml of ethanol, two drops of HNO_3, 0.5 g of hexadecanol, 0.4 ml of glycerol, and 57 μl of hydrazine. This mixture was stirred and refluxed at 60 °C for three days. The absorption band of the colloidal solution was found around 420 nm. This plasmon band is

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a characteristic of Ag^0 colloids [5–10], and its confinement leads to strong nonlinearities.

The synthesis of SiO_2–Ag^0 was prepared by mixing in an Erlenmeyer flash the aqueous ammonia (11.9 ml of NH_3 at 29%) and the 88.1 ml of ethanol. This solution was then stirred in a water bath at 20 °C. After this, 5 ml of solution containing the silver colloids were mixed for 10 min, and then 3.6 ml of tetraetoxilsilano was added under vigorous stirring. Gentle stirring was continued for 15 h, and the solvent was removed by centrifugation at 3000 rpm for 30 min. The diameters of the particles ranged from 200 to 400 nm.

The FTIR analysis was carried out in a FTIR Perkin Elmer Paragon 1000 Spectrometer, where the samples were prepared as KBr disks. The absorption spectra were performed using an UV-Visible spectrometer Cary-5 XRD. The X-ray diffraction patterns of SiO_2 and SiO_2–Ag^0 were obtained by a Siemens D-500 diffractometer coupled to a molybdenum anode tube. The X-ray spectra were determined in the 2θ refraction range extending from 0.4° to 10°. The intensity values were read at $\Delta(2\theta)$ intervals of 0.010° by a time step of 1.2 s. The transmission electron microscopy (TEM) measurements were carried out in a JEM-2010F FASTEM electron microscope operating at 200 kV. The samples used for TEM were prepared by dissolving them with isopropanol, followed by redeposition on a 300 mesh copper grid, and subsequently air dried before being analyzed by the TEM.

The reduction of Ag^+ ions in CH_3CH_2OH results in the fast formation of nanoparticles of Ag^0 [8]. The standard reduction potential of Ag^+ is carried out in ethanol. The formation of metal particles in alcohol is spontaneous at a lower OH- concentration, because these solvents are stronger reductants than water. Fig. 1 shows clearly the intensity of the absorption peak at 420 nm. The presence of this peak is consistent with the surface plasmon resonance (SPR) of silver nanoparticles [5–10], which is formed in solution. The TEM image of Ag^0 nanoparticles is shown in the inset of Fig. 1. The micrographs indicated the formation of Ag^0 nanoparticles dispersed in the substrate with a diameter size between 2 and 12 nm.

The TEM images for SiO_2 show submicrospheres with a diameter ranging from 200 to 400 nm. TEM images of SiO_2–Ag^0 are shown in Fig. 2. The spheres of SiO_2 are quite symmetrical and showing silver nanoparticles aggregates. The picture clearly reveals the aggregated nature of the Ag^0 nanoparticles into the SiO_2 submicrospheres (<12 nm). When these nanoparticles were excited with light at a wavelength of 320 nm, the detected emission was in the range of 350–550 nm, while in the case of

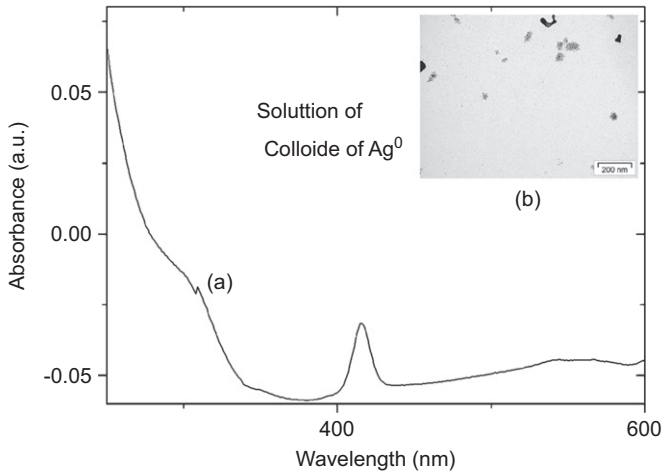

Fig. 1. (a) Absorption UV–Vis nanoparticles Ag^0. (b) Transmission Microscope Image (TEM) of nanoparticles Ag^0 in solution.

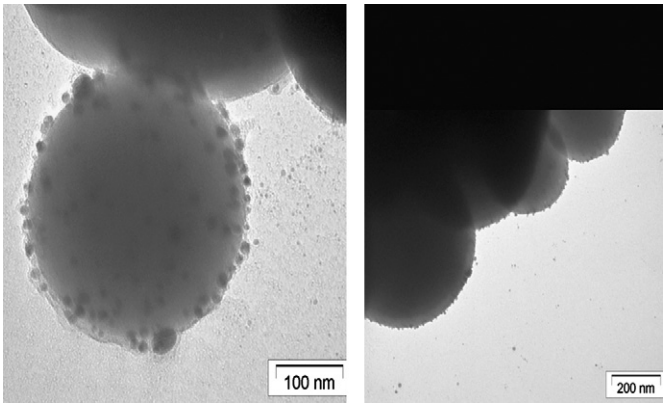

Fig. 2. Images obtained by transmission microscopy images (TEM) of SiO_2 submicrospheres with silver nanoparticles (SiO_2–Ag^0).

an excitation source centered at 380 nm the emission spectrum showed a peak around 420 nm.

The FTIR spectra of SiO_2 and SiO_2–Ag^0 showed a band at 3745 cm^{-1} due to the symmetric stretching vibration mode O–H of the isolated terminal silanol Si–OH group. We also observed a band at 3400 cm^{-1}, which is due to the absorption of hydrogen-bonded water molecule, and the band at 1631 cm^{-1} which is due to flexion vibration of O–H water molecule. Particles in these nano-dimensions have very particular properties well described by the corresponding Mie Electromagnetic theory [11], in particular metallic particles [12]. However, in the range of a few nanometers ~10 nm they show a characteristic nonlinear behavior that arises from the confinement of its plasmon [13], a size-dependent feature, extensively discussed by Uchida et al. [13].

In order to study the isolated nanoparticles, a thin film of such nanoparticles was prepared. The synthesis of the film with silver nanoparticles was obtained by immersion of a microscope slide into the silver nanoparticles solution. The immersion speed was 0.25 cm/min and the plates were dried by exposure to the atmosphere. The microscope slides were prepared with a pH solution (HCl, HO_2) and then dried with high purity nitrogen. This resulted in a film where the nanoparticles were not only embedded, but they were kept separated and unable to change its size. This is a common scheme used to study nanoparticles embedded in different materials such as glass [13], and polymer films [14]. However, the majority of the methods to measure the nonlinear optical response of nanoparticles have used four wave mixing [15], third harmonic generation [16], and pump probe and Optical-Kerr-shutter (OKS). On the other hand, the Z-scan technique is a simple method which can provide the sign and the magnitude of the nonlinearity and has been successfully used to study the nonlinear behavior of 1D MPC [17]. In the typical Z-scan experimental setup, the transmittance T is measured as a function of the sample position (Z) and the orientation, and the nonlinearity sign is obtained graphically. We selected this method because of their simplicity, the good optical quality and convenient preparation of our samples (no highly scattering media).

In the experimental setup we used a 20 mw CW HeNe and a pulsed Nd–YAG lasers (both at 543 nm wavelength), the focal length was 7.5 cm and a beam radius of 3 mm which corresponds to a diffraction length of 0.432 mm. The sample thickness was only 125×10^{-6} m, which can be considered as a thin nonlinear medium. Fig. 3 shows experimental results of the silver nanoparticles' nonlinear refractive index which were obtained by using a pinhole in the intensity detector at the Z-scan experimental set-up. The points represent the experimental data while circle, triangular and continuous line represents; pure refraction, high

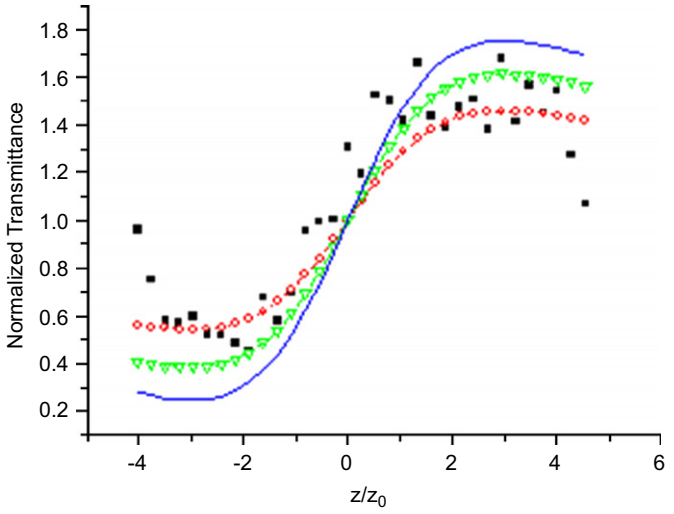

Fig. 3. Z-scan graphs for nonlinear refraction index obtained from Silver nanoparticles with three different theoretical approximations.

precision and out of axis approximations, respectively. The graph clearly exhibits a positive sign for the nonlinearity of silver. Using the models showed by Chapple et al. [18], we fit them with the experimental obtained data and we estimated the value of the nonlinear refractive index for the film with silver nanoparticles as $5.0115 \times 10^{-10}$and 0.01948 m/W for the value for the nonlinear absorption coefficient. These results, on the one hand, are consistent with the nonlinearities of silver nanoparticles [11] and those dispersed in a glass reported in Table 2 by Uchida et al. [13], once we realize that we have a broad sample of silver nanoparticles between 2 and 12 nm.

3. Conclusions

The synthesis procedures for SiO_2, Ag^0 and SiO_2–Ag^0 nanoparticles, the basic elements of much more complex structures, are discussed as well as their analysis. The signature provided by the silver plasmon is readily noticeable in the silver nanoparticles and also in the SiO_2–Ag^0 composite nanoparticles. The samples exhibited a positive nonlinear refractive index and a nonlinear absorption coefficient with 5.0115×10^{-10} and 0.01948 m/W, respectively. Our results demonstrate that the nanospheres composite exhibited quite convenient features for the design of nonlinear photonic structures with metallic inserts.

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