

Photoconductivity on nanostructured sol-gel thin films with silver nanoparticles

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ABSTRACT

2d-hexagonal nanostructured sol-gel thin films were prepared by dip-coating method. A neutral surfactant Brij58 was used as template to produced channels into the film. The structure was identified by X-ray diffraction and TEM. Silver nanoparticles were obtained by spontaneous reduction process of Ag^+ ions to Ag^0 at room temperature. A broad band located at 430 nm was detected by optical absorption; it corresponds to the surface plasmon. Photoconductivity studies were performed on films with ions and with silver nanoparticles to characterize their mechanisms of charge transport in the darkness and under illumination at 420 and 633 nm wavelengths. Straight lines showing an ohmic behavior fit the experimental data. Films without colloids possess normal photoconductivity behavior. But films with colloids present an abnormal response. Transport parameters were calculated. The films with silver nanoparticles exhibit a photovoltaic effect stronger than the films without nanoparticles, except to high concentrations. A theoretical model is proposed to predict these processes as function of the silver concentration.

KEYWORDS: photoconductivity, nanoparticles, dip-coating, thin films, surfactant, surface plasmon.

I. INTRODUCTION

To synthesize nanostructured sol-gel thin films four reagents are generally required: water, a surfactant, a silica source (such as TMOS or TEOS), and a catalyst (as HCl). Nanostructured sol-gel thin films use surfactants to template or provide ordered structure to the amorphous silica matrix. As example neutral block copolymers can be used. These copolymers are macromolecules consisting of two or more different polymer blocks together¹. Each block is a sequence of typically around a hundred to a thousand monomers.

Studies of photovoltaic and photoconductive properties in Ag doped glasses have been done because of their ionic nature². These kinds of materials exhibit electrical and optical properties, characteristic of ionic conductors and semiconductors. That is, the electrical conductivity is governed by Ag^+ ionic conduction since the hole conductivity is substantially smaller and electron conductivity is not detected.

In this work, nanostructured sol-gel thin films doped with silver nitrate were prepared by dip coating method using a neutral oligo (ethylene oxide) surfactant (Brij58) as template for silica polymerization in the synthesis of uniformly distributed silver-ion-containing nanostructured silica material. During the deposition by dip coating, a layer of solution is dragged onto the substrate surface. The structure of the film forms via evaporation-induced self-assembly³ for which the solvent evaporation simultaneously induces the formation of micelles. This implies that the organization, condensation, and drying of the films occur in the few minutes following the substrate withdrawal from the sol. A 2d-hexagonal phase⁴ was detected by X-ray diffraction.

Optical absorption studies were done to follow the growth of a broad absorption band in the visible region of the spectrum between 400 and 500 nm due to the plasmon mode of metallic silver, spontaneously generated at room temperature. They were obtained as function of time.

Photoconductivity studies were done on the nanostructured sol-gel films with nanoparticles to determine the charge transport parameters. A theoretical model was fitted to the experimental data taking into account the molar concentration of Ag and the presence on the silver colloids in the films.

II. EXPERIMENTAL

Glass substrates were boiled in an acidic solution of sulphuric acid with hydrogen peroxide. Films were dip coated to the glass substrates at rate of 3.5 cm/min (see Figure 1). The films were drawn with the equipment described previously that uses hydraulic motion to produce a steady and vibration-free withdrawal of the substrate from the sol⁵. Convection-free drying was critical to obtain high optical quality films.

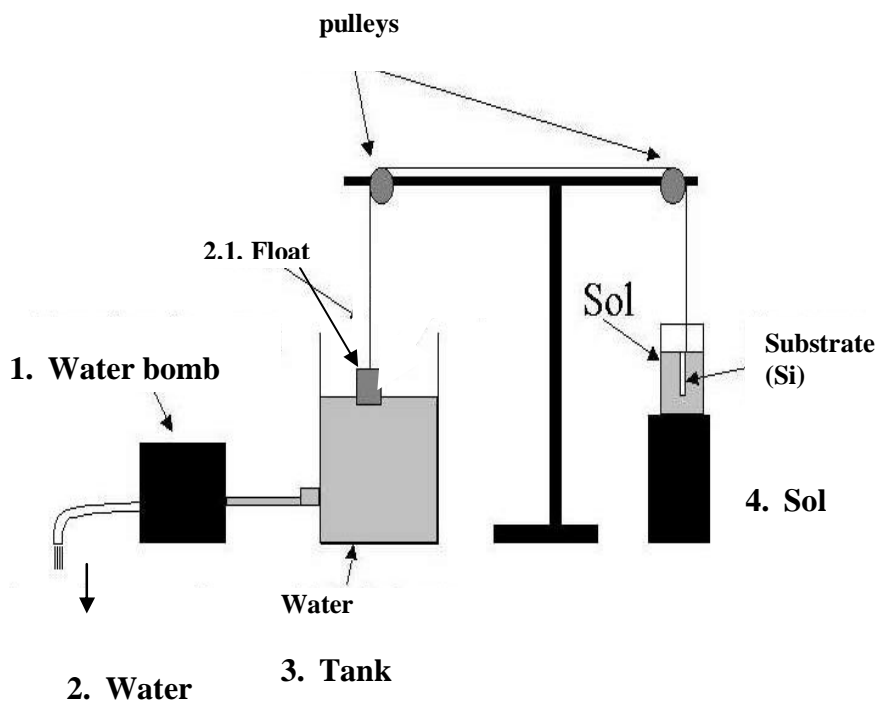


Figure 1. Experimental apparatus to prepare the mesostructured thin films by dip coating method.

All reagents are Aldrich grade. An initial solution was prepared with AgNO_3 (silver nitrate) dissolved in a small quantity of deionized water and nitric acid. Then was added 1 g of methanol, 5.4 g of TMOS (Tetra methyl orthosilicate), and 1.3-4 g of the neutral surfactant $\text{C}_{16}\text{H}_{33}\text{PEO}_{20}$. This initial solution was mixed and heated to 50-70 °C for 20 minutes to homogenize the mixture. The final concentrations were $\text{AgNO}_3/\text{C}_{16}\text{H}_{33}\text{PEO}_{20} = 0.3\text{-}1.0$ molar ratio.

The structure of the final films was characterized with X-ray diffraction (XRD) patterns. These patterns were recorded on a Siemens D500 diffractometer using Ni-filtered $\text{CuK}\alpha$ radiation with an integration time of 1 sec at low angle. Transmission electron microscopy (TEM) was taken with a JEOL 4000EX high-resolution TEM (HRTEM) at 400kV with 0.17 nm resolution.

For photoconductivity studies⁶ silver electrodes were painted on the sample. It was maintained in a 10^{-5} Torr vacuum cryostat at room temperature in order to avoid humidity. For photocurrent measurements, the films were illuminated with light from an Oriel Xe lamp passed through a 0.25m Spex monochromator. Currents were measured with a 642 Keithley electrometer connected in series with the voltage power supply. The applied electrostatic field E was parallel to the film and perpendicular to the illumination. Light intensity was measured at the sample position with a Spectra Physics 404 power meter⁶ (Figure 2).

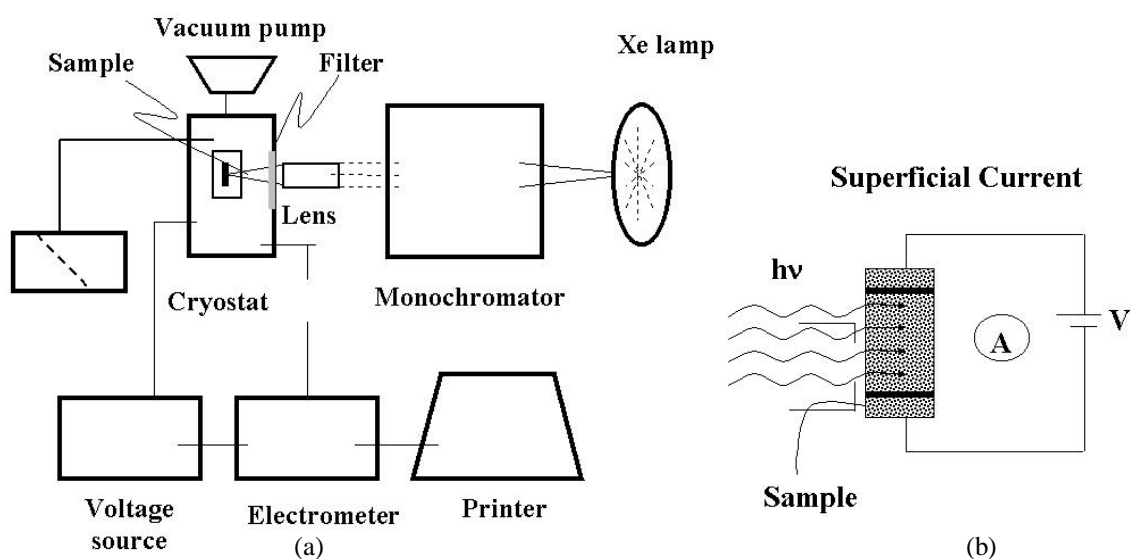


Figure 2. (a) Schematic diagram of the photoconductivity technique. Surface current was produced on the thin film when an electric field was applied it as it is shown in (b).

III. RESULTS

Three kind of results were obtained. The first one refers to the absorbance behavior of the films as function of the $\text{AgNO}_3/\text{Brij58}$ molar ratio, at the wavelength in which Ag surface plasmons exhibit their main optical absorption contribution. The second kind of results deals with the photoconductivity of the films, either when they have Ag colloidal **nanoparticles** as when they mainly have Ag^+ **ions**. And the third one comes from the comparison between the photovoltaic parameters of the films with nanoparticles.

III. 1. Characterization.

Samarskara et al. ⁴ reported a lyotropic liquid crystalline phase of oligo (ethylene oxide) surfactants which house Ag⁺ ions in the hydrophilic ethylene oxide head group and allow Ag⁺ ions to distribute uniformly into the channels of mesoporous silica materials. We used the same recipe to prepare our films deposited on glass slides at different concentrations of AgNO₃/Brij58 using the block copolymer Brij58 as template to form these channels. Figure 3 (a) shows the X-ray pattern from film with AgNO₃/Brij58 molar ratio equal to 0.7. The peak at $2\theta = 1.649^\circ$, or a d-spacing of 54 Å, corresponds to the (100) peak of the 2d-hexagonal-phase structure. Transmission electron microscopy (TEM) was used to image films containing the silver nanoparticles. The Figure 3 (b) shows the hexagonal array formed.

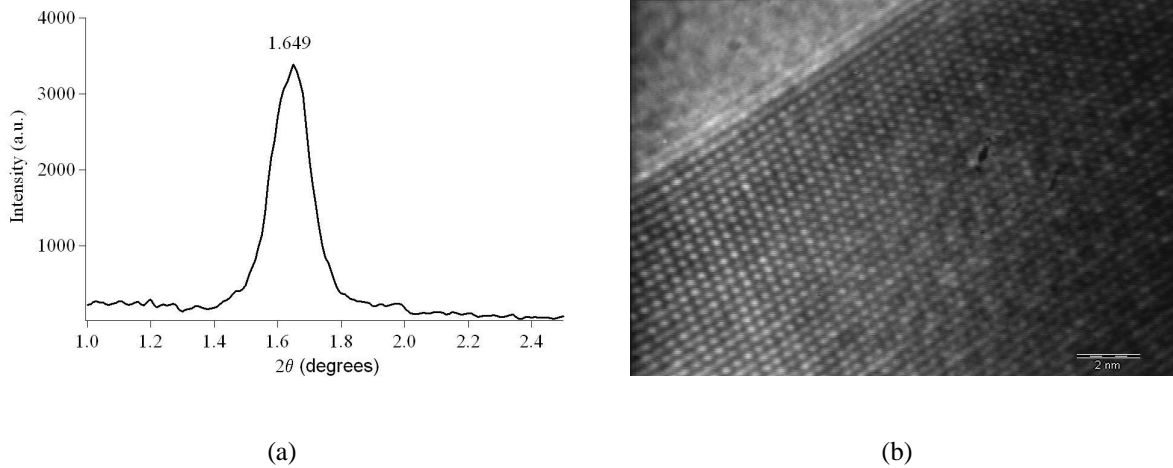


Figure 3. (a) Low angle XRD pattern from sol-gel nanostructured thin film with AgNO₃/Brij58 = 0.7 molar ratio. (b) TEM image from sol-gel nanostructured thin film with AgNO₃/Brij58 = 0.7 molar ratio, it shows the hexagonal array formed into the film using the neutral surfactant Brij58.

III. 2. Absorbance.

The presence of Ag colloidal nanoparticles in the films is clearly evidenced by means of the optical absorption spectroscopy. A maximum in the optical absorption spectrum exists when there are colloids in the sample. This maximum appears at an illumination wavelength of around 400 nm. The exact wavelength at which there is the maximum absorbance depends on several system features, for example it depends on the nanoparticles size and shape distribution, and it also depends on the dielectric behavior of the nanoparticles surrounding medium. In Figure 4 the absorption coefficient of the films was plotted as a function of the AgNO₃/Brij58 molar ratio.

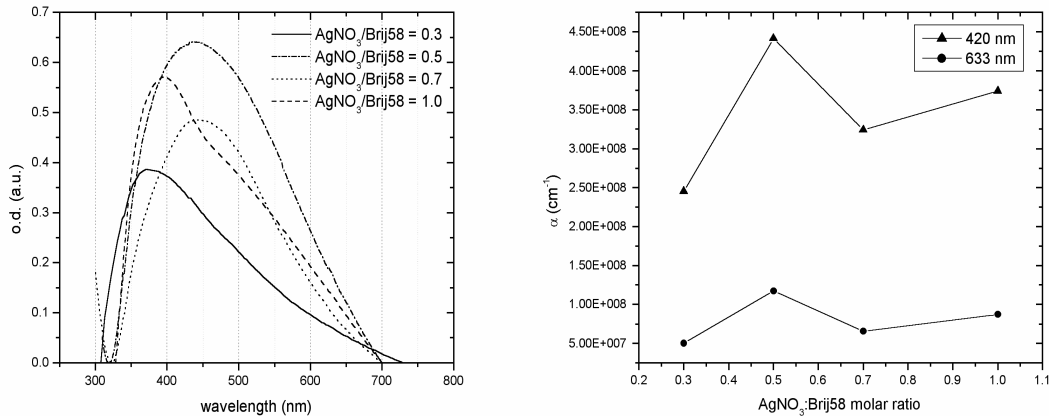


Figure 4. (a) Optical absorption spectrum for different AgNO₃/Brij58 molar ratios. (b) Absorbance as function of the AgNO₃/Brij58 molar ratio for two different illumination wavelengths: 420 nm (plasmon absorption) and 633 nm (any other).

There is an evident change in the samples spectra with respect to the different AgNO₃/Brij58 molar ratios. It would be expected that as the molar ratio increases the absorbance increases too, but in Figure 4 the absorbance is larger for a molar ratio equal to 0.5. However AgNO₃ concentration is not the same that Ag⁰ nanoparticles concentration. In consequence there is an optimum AgNO₃/Brij58 molar ratio for which there are more Ag⁰ nanoparticles generated. In our case a molar ratio equal to 0.5 is optimum.

Another feature of the Figure 4 spectra is the shift of the absorption peak. As the molar ratio increases the absorption peak has a red shift, but for the molar ratio equal to 1.0 the peak return to a wavelength slightly larger than that of molar ratio equal to 0.3. The nature of these shifts is still under study.

III. 3. Photoconductivity.

The photoconductivity studies are based on the stationary current density J vs. applied electric field E . Figure 5 shows these experimental data. It is usually accepted that dark conductivity and photoconductivity is produced by hopping mechanism in these insulating materials.

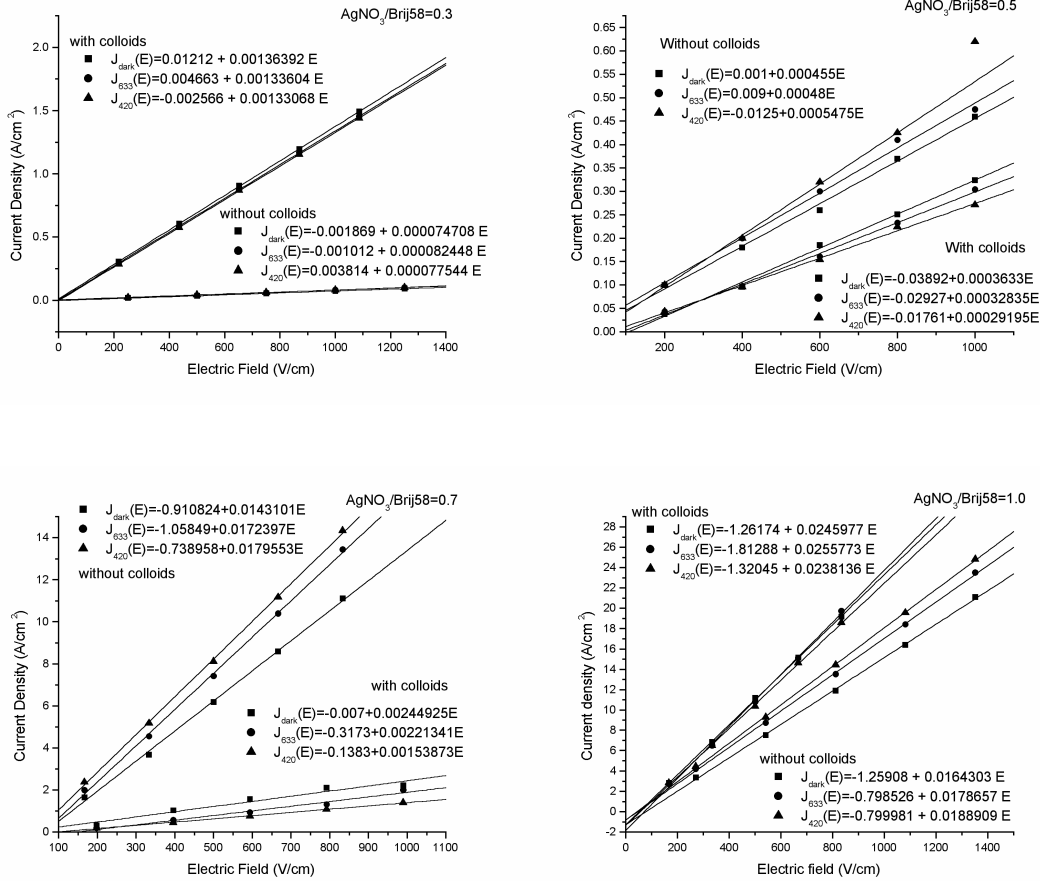


Figure 5. J vs. E plots for all the considered $AgNO_3/Brij58$ molar ratios.

These experimental data follows a linear dependence as can be seen in Figure 5. It means they have an ohmic behavior. From these data the photoconductivity and photovoltaic parameters can be obtained through the equation (1).

$$J = \frac{e\phi l_0}{h\nu} \alpha I + \left(en\mu + \frac{e\phi\mu\tau}{h\nu} \alpha I \right) E, \quad (1)$$

where e is the fundamental electrostatic charge, ϕ is the photogeneration quantum efficiency, l_0 is the charge carrier mean free path, h is the Planck's constant, ν is the frequency of the illumination light, α is the absorbance of the film at the illumination frequency, I is the illumination intensity, n is the charge carrier density, μ is the charge carrier mobility and τ is the charge carrier mean lifetime.

The first term in equation (1) refers to the photovoltaic effect, the second term ($en\mu$) is the dark conductivity and the third term is the photoconductivity. The parameters ϕl_0 give information about the photovoltaic effect, i.e., how much voltage is generated in the material under illumination; and the parameters

$\phi\mu\tau$ give the information related to the photoconductivity, i.e., how much the conductivity changes under illumination.

Some differences were observed from Figure 5 in the electronic transport properties between samples with silver ions and with silver colloidal nanoparticles. The first observation is related with the dark conductivity. As function of the $\text{AgNO}_3/\text{Brij58}$ molar ratio the dark conductivity increases in all the cases, but it is different for the two kind of samples: with and without nanoparticles.

Figure 6 shows the data obtained from Figure 5 for the dark conductivity and for the photoconductivity of both kind of films.

The conductivity in the films with silver nanoparticles is related with the Ag electrons, but in the films without nanoparticles the concentration of Ag^+ ions is very large, in consequence the conductivity in these last films must be mainly ionic. The first kind of conductivity is benefited by the increase in the Ag concentration, the second one also is benefited by the increase in the Ag^+ concentration. But in the ionic conductivity with a high concentration of ions they may have a mutual electrostatic inhibition. In consequence an increment in Ag^+ ions concentration does not necessarily produces an increment in the dark conductivity.

Because the conductivity is directly proportional to the charge carriers' concentration, the next differential equation describes how the conductivity (σ) depends on the Ag concentration (x).

$$\frac{d\sigma(x)}{dx} = r\sigma(x), \quad (2)$$

with r a film constant. The solution to equation (2) is an exponential function of the concentration.

But for the ionic conductivity the equation must consider the increase of electrostatic interaction between ions as the ions concentration increases, so we have the next differential equation.

$$\frac{d\sigma(x)}{dx} = r\sigma(x) \left(\frac{K - \sigma(x)}{K} \right), \quad (3)$$

with K the maximum possible conductivity. The solution to equation (3) is a logistic function of the concentration.

The continuous lines in Figure 6 fit the experimental data for the dark conductivity, by means of equations (2) and (3).

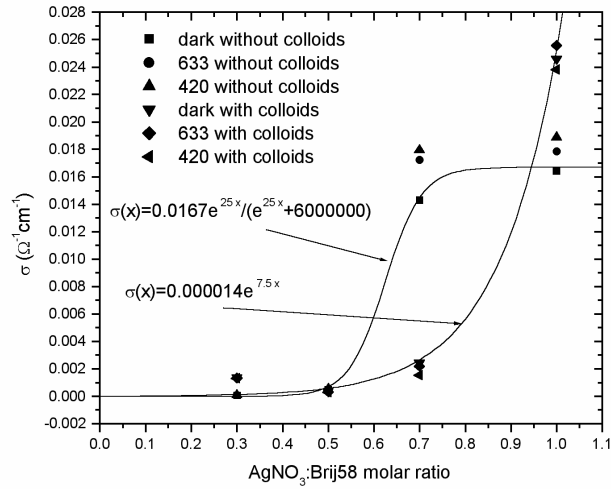


Figure 6. Conductivity vs. $\text{AgNO}_3/\text{Brij58}$ molar ratio experimental data for films with and without silver nanoparticles. Continuous lines fit dark conductivity employing equations (1) and (2).

From Figure 6 is clear that the photoconductivity follows the same behavior of the dark conductivity as function of the concentration. That means, the differences between both are no so big, as is clearly shown in Figure 5. But again the photoconductivity is very different in each case: with and without silver colloidal nanoparticles. If the film does not have nanoparticles then the photoconductivity is bigger than the dark conductivity, but if the film has nanoparticles then the photoconductivity can be shorter than the corresponding dark conductivity as can be clearly seen in Figure 5. The calculated values for the photoconductive parameters $\phi\mu\tau$ as function of $\text{AgNO}_3/\text{Brij58}$ concentration were plotted in Figure 7. They were obtained in the films with colloids using the equation (1) and the method described by García et. al.⁹, which consists in an adequate comparison between the experimental data under dark conditions and those under illumination, with data from Figure 5.

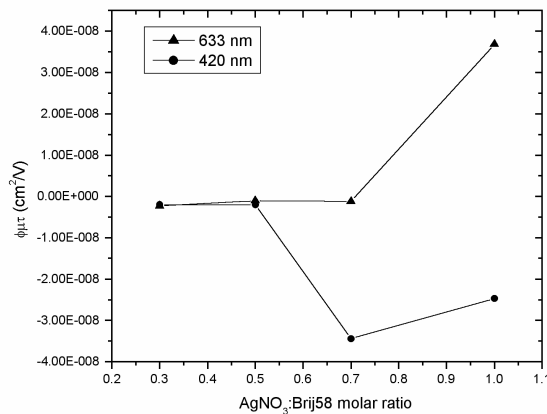


Figure 7. $\phi\mu\tau$ transport parameters vs. $\text{AgNO}_3/\text{Brij58}$ molar ratio plot for films with Ag colloidal nanoparticles. The illumination was carried out at two different wavelengths: 633 nm and 420 nm.

From the Figure 7 is clear that in the case in which the films are illuminated with a wavelength of 633 nm, far from the plasmon peak, the value for $\phi\mu\tau$ is positive and increases as the molar ratio increases, just as is expected from the films without nanoparticles. That is, at wavelengths different to the plasmon absorption peak, the films with nanoparticles exhibit photoconductive values as if there were not nanoparticles. But in the case in which the films are illuminated with a wavelength near the maximum absorption peak (420 nm), the silver nanoparticles play an important role, they induce a decrement in the conductivity. That decrement is such that the parameters $\phi\mu\tau$ take large negative values as the molar ratio increases.

III. 4. Photovoltaic parameters.

The photovoltaic parameters ϕl_0 can be also calculated employing equation (1) and data from Figure 5. The behavior of the photovoltaic parameters ϕl_0 as function of the $\text{AgNO}_3/\text{Brij58}$ molar ratio is shown in Figure 8.

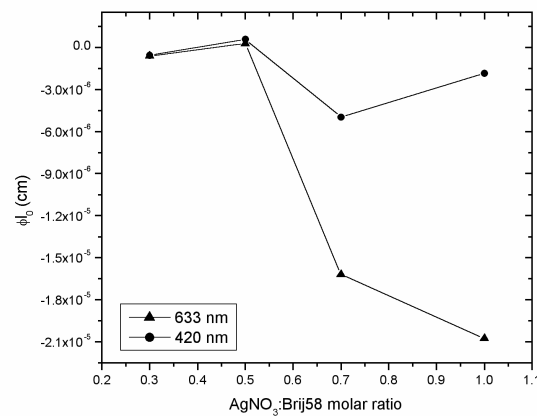


Figure 8. Photovoltaic transport parameter ϕl_0 vs. $\text{AgNO}_3/\text{Brij58}$ molar ratio plot for films with Ag colloidal nanoparticles. The illumination was carried out at two different wavelengths: 633 nm and 420 nm.

From Figure 8 is clear the existence of an important photovoltaic response for large molar ratio values. But the strongest response is observed under illumination at a wavelength far from the plasmon absorption peak. Table I contains all the electronic transport parameters obtained for the films with nanoparticles.

Table I. Obtained photovoltaic and photoconductivity parameters on films with nanoparticles.

Sample	Parameter	633 nm	420 nm
$\text{AgNO}_3/\text{Brij58}=0.3$	ϕl_0 (cm)	-6.1×10^{-7}	-5.7×10^{-7}
	$\phi\mu\tau$ (cm^2/V)	-2.3×10^{-9}	-2.0×10^{-9}
$\text{AgNO}_3/\text{Brij58}=0.5$	ϕl_0 (cm)	2.8×10^{-7}	5.9×10^{-7}
	$\phi\mu\tau$ (cm^2/V)	-1.0×10^{-9}	-2.0×10^{-9}
$\text{AgNO}_3/\text{Brij58}=0.7$	ϕl_0 (cm)	-1.6×10^{-5}	-5.0×10^{-6}
	$\phi\mu\tau$ (cm^2/V)	-1.2×10^{-9}	-3.4×10^{-8}
$\text{AgNO}_3/\text{Brij58}=1.0$	ϕl_0 (cm)	-2.1×10^{-5}	-1.8×10^{-6}
	$\phi\mu\tau$ (cm^2/V)	3.7×10^{-8}	-2.5×10^{-8}

IV. CONCLUSIONS

Nanostructured sol-gel thin films were produced with an excellent 2D hexagonal phase. The absorption spectrum shows the characteristic band from surface plasmon mode at 420 nm in films with nanoparticles. The AgNO₃/surfactant molar ratio plays an important role in the optical and in the transport properties of the films. The films with and without nanoparticles exhibit very different physical behaviour. The AgNO₃/Brij58 molar ratio modifies the absorbance of the silver surface plasmon and the position of its maximum absorption wavelength. Charge conductivity as function of the AgNO₃/Brij58 molar ratio exhibits different responses for the two kind of films. The photoconductivity in the films with nanoparticles inhibit the charge transport, but in the films without nanoparticles the behaviour is as usual: conductivity increase its value under illumination. The photovoltaic effect in the films with nanoparticles is larger when the sample is illuminated with a wavelength far from the plasmon absorption peak. Exponential and logistic equations fit these results.

V. REFERENCES

1. D. Grosso, A.R. Balkenende, P.A. Albouy, A. Aryal, H. Amenitsch, F. Babonneau "Two-Dimensional Hexagonal Mesoporous Silica Thin Films Prepared from Block Copolymers: Detailed Characterization and Formation Mechanism". *Chem. Mater.* **13**, 1848-1856 (2001).
2. D. Sharma, R.K. Shukla, A. Kumar. "Transient photoconductivity in amorphous thin films of Se₇₅ Te₂₀ Ag₅". *Thin Solid Films* **357**, 214-217 (1999).
3. Garcia, J.A.; Valverde, G.; Zink, J. "Using Carbazole as a Structural Modifier of CTAB-Templated Silicate Sol-Gel Thin Films". *Langmuir* **19**, 4411-4414 (2003).
4. O. Samarskaya, O. Dag. "Silver Nitrate/Oligo(ethylene Oxide) Surfactant/Mesoporous Silica Nanocomposite Films and Monoliths". *J. Colloid and Interf. Sci.* **238**, 203-207 (2001).
5. F. Nishida, et al. "In situ fluorescence probing of the chemical changes during sol-gel thin film formation". *J Am. Cer. Soc.*, **78**, 1640-1648 (1995).
6. J. García M., A. Mondragón, J. M. Hernández, J. L. Maldonado R. "Photocurrent determination of charge transport parameters in KNbO₃:Fe³⁺". *Op. Mat.* **3**, 61 (1994).

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