

SILVER NANODISPERSIONS IN ORGANIC-INORGANIC FILMOGENE HYBRIDS

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Hybrid materials containing methyltriethoxysilane (MeTES), with and without 3-(trimethoxysilyl)-1-propanthiol (HSTMS), in the presence of colloidal silver powder and of some cationic dyes were prepared by sol-gel method. Aqueous dispersions of colloidal silver were prepared at three concentrations (0.1%, 0.5% and 1%) and were analyzed by dynamic light scattering (DLS). It was observed that the particles distributions were bimodal, unaffected by concentration. The average diameters of the two populations of particles were 150 nm and 35 nm, respectively. After evaluation of Rhodamine B behavior in alcohol/water system, we found that this dye present hydrophobic association in both, solution and organic-inorganic hybrid materials. This fact has as result simultaneous presence of the monomer and dimer forms of the molecule.

INTRODUCTION

The film formation by sol-gel is a very complex process.¹ In previous studies we showed the modification of the properties of such films that depend on the components nature.^{2,3} The organic-inorganic hybrid films, which contain silver nanoparticles, attract a special interest because of their antimicrobial properties.⁴⁻⁷ These type of materials can be used for biosensors, membranes, electro-catalysis, optics.⁸⁻¹¹

The aim of this work is to synthesize and evaluate the properties of some hybrid films obtained by the sol-gel process. As sol-gel precursors we used methyltriethoxysilane (MeTES) and 3-(trimethoxysilyl)-1-propanthiol (HSTMS), when mentioned (see Tab.1). The films were prepared in the presence of a colloidal silver powder and of some cationic dyes and the synthesis procedure has been described elsewhere.^{2,3} Using HSTMS, the morphology of the hybrids obtained with another partners is changing and the silver nanoparticles bonding is enhanced.¹²⁻¹⁵

RESULTS AND DISCUSSION

By scientific and applicative reasons, were studied different dyes incorporated in hybrid materials.^{16,17} In our previous studies we showed that Rhodamine B (RhB) dye gives spectral modifications depending on the alkyl trialkoxydic components polarity.² This dye presents hydrophobic associations both, in solutions¹⁸⁻²⁰ and in the organic-inorganic hybrid materials.²⁰⁻²² The effect is the simultaneous presence of both monomer and dimer forms of the molecule in the reaction medium. Dimer's presence is much lower in organic-inorganic hybrid materials.²⁰

The dyes adsorption on silver nanoparticles induces a modification of the spectral characteristics.²³ By this reason, we studied the influence of the silver nanoparticles on the spectral behavior (UV-VIS) for Rhodamine B (RhB), Kristallviolett (CV) and Malachite green (VM), two cationic dyes, and Methylenblau BP (BM), dye which has a sulfur atom in its structure that can interact with particles incorporated in system.²⁴

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The silver nanoparticles dispersed in liquid environment give UV-VIS absorption (~ 400 nm), silver's wavelength (λ_{\max}) depending on dimensions, environment polarity and stabilizers nature.²⁵⁻²⁸ The wavelength shifts to higher values (red shift) due to increase of particles size, decrease of medium polarity and stabilizers presence. The same conclusion was also observed for the case of organic-inorganic hybrids doped with silver nanoparticles.^{5, 11, 29}

According with data published before, ensue that UV-VIS spectroscopy is an efficient method to show polarity modifications of the dispersion medium, both for dyes and for silver nanoparticles.^{5, 11, 18-29} In a previous paper we demonstrated that through UV-VIS spectroscopy can be proved the nanostructuring of ethanol-water binary system and the tendency of a component to form hydrophobic association, depending on partner's

ratio.³⁰ Following these results, the goal of the present study is to investigate the modifications induced by the ethanol/water mixture over UV-VIS spectra of RhB.

After evaluation of Rhodamine B behavior in alcohol/water system, we found that this dye present hydrophobic association in solution as well as in organic-inorganic hybrid materials. The consequence is the simultaneous presence of the monomer and dimer forms of the molecule. At $f = 0.166$ (where f is the molar ratio of water in alcohol) it was observed the critical concentration, where the alcohol molecules auto-associate (figures 1-4). In alcohol-water system, the wavelength variation is due to alcohol nanostructuring.³⁰ Due to ethanol molecules auto-assembling, hydrophobic areas that permit the dissolution of the RhB are formed.³¹

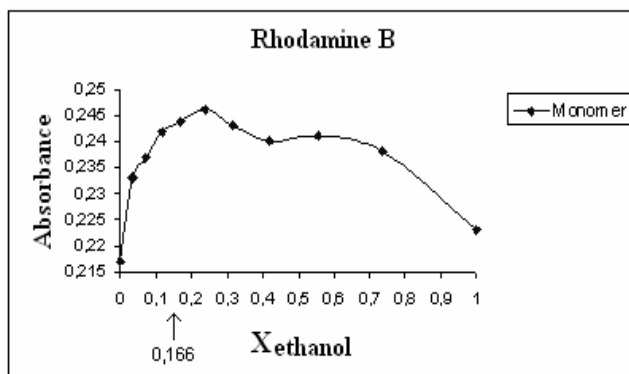


Fig. 1 – The absorbance changing of the emission peak for UV-VIS spectra of Rhodamine B in alcohol/water system, as function of alcohol molar ratio (for monomer).

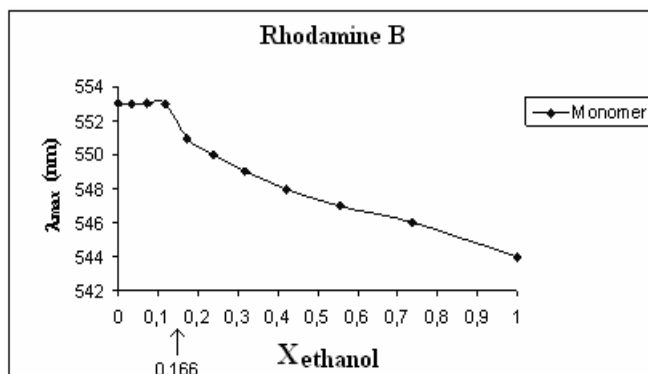


Fig. 2 – The wavelength changing of the emission peak for UV-VIS spectra of Rhodamine B in alcohol/water system, as function of alcohol molar ratio (for monomer).

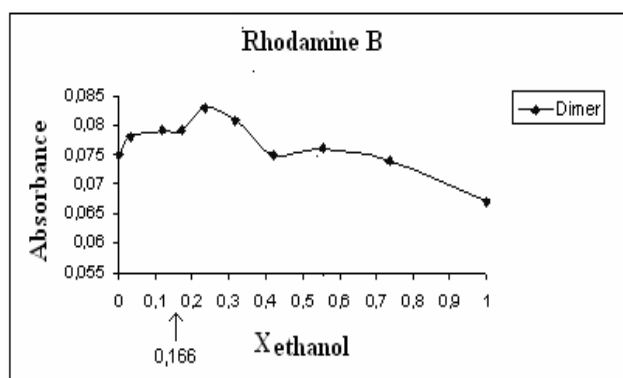


Fig. 3 – The absorbance changing of the emission peak for UV-VIS spectra of Rhodamine B in alcohol/water system, as function of alcohol molar ratio (for dimer).

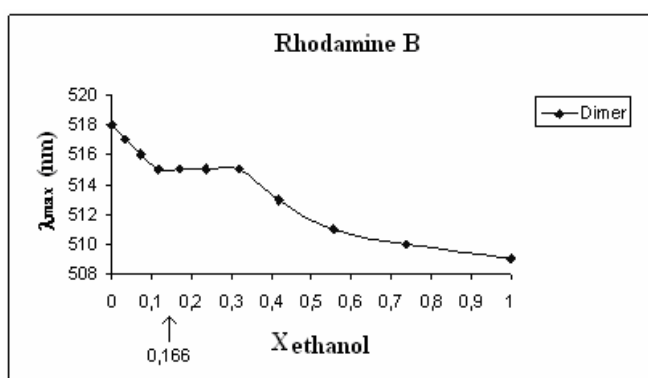


Fig. 4 – The wavelength changing of the emission peak for UV-VIS spectra of Rhodamine B in alcohol/water system, as function of alcohol molar ratio (for dimer).

According to the DLS measurements of the colloidal silver powder, it was observed that the particles distributions were bimodal, unaffected by

concentration. The average diameters of the two particles populations were 150 nm and 35 nm respectively (figure 5).

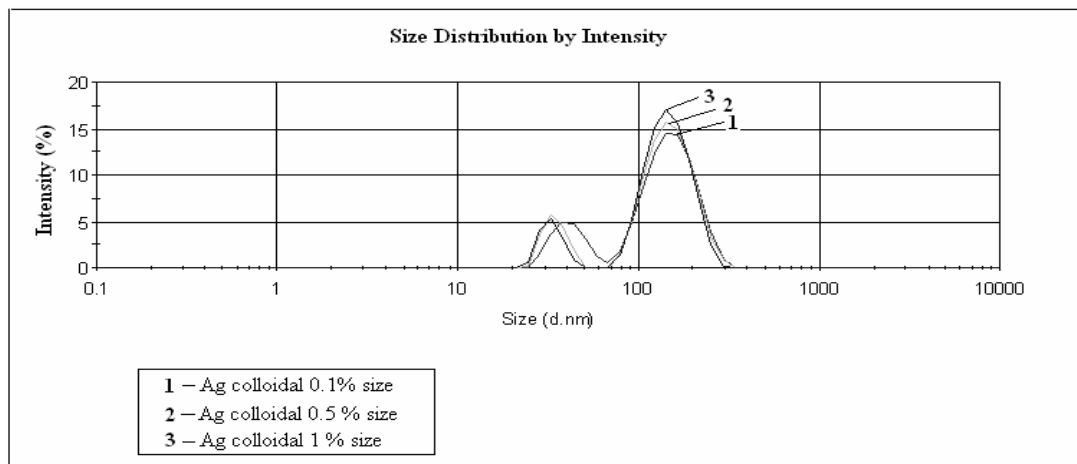


Fig. 5 – Size distribution by intensity for the colloidal silver powder in water, at different concentrations.

After evaluation of FT-IR spectra of the colloidal silver doped films (figures 6 and 7), were not observed significant modifications, at the used concentrations of colloidal silver. For all samples,

the Si-O-Si group gives a strong absorption band in the spectral region between $1000\text{--}1200\text{ cm}^{-1}$ (figure 6). The Si-O-Si symmetric stretching gives a contribution at $\sim 770\text{ cm}^{-1}$.

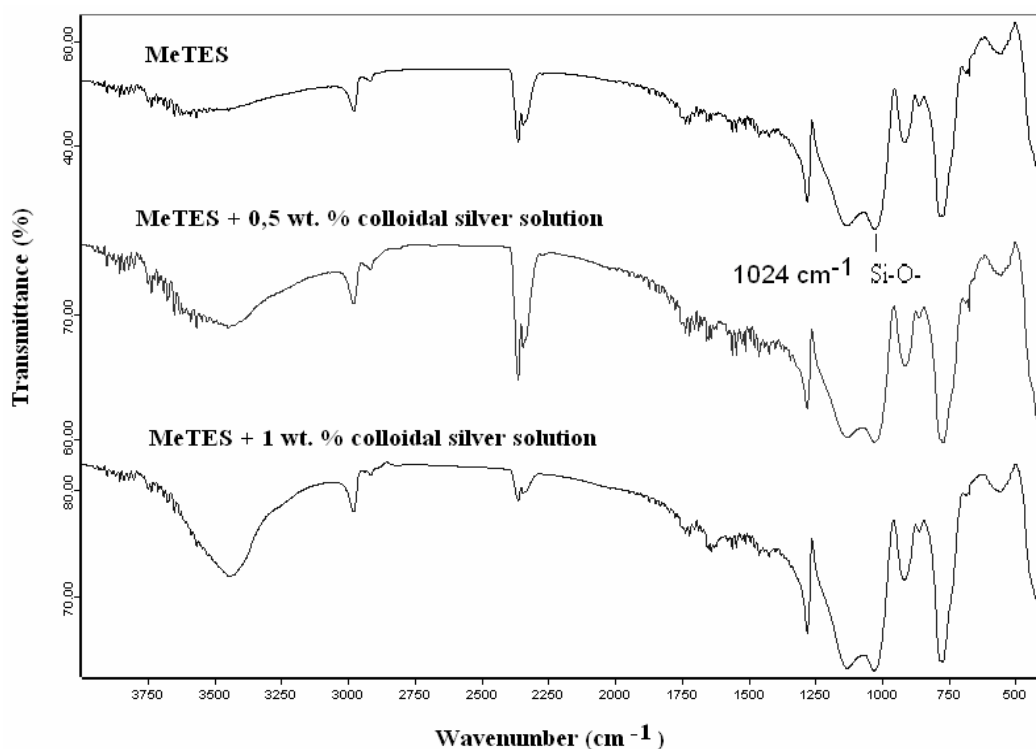


Fig. 6 – FT-IR spectra for MeTES – based hybrids, doped with different colloidal silver solutions.

For hybrids with MeTES and HSTMS, doped with different colloidal silver solutions, a strong absorption band at $1000\text{--}1200\text{ cm}^{-1}$, corresponding to the Si-O-Si group, can be observed. Another important absorption band can be found at 2933 cm^{-1} , corresponding to the RS group (figure 7).

The UV-VIS spectra show the modification of the absorption domain for colloidal silver, as function of

silver nanoparticles concentration (figures 8 and 9). The hybrids present UV-VIS absorption at $\sim 400\text{ nm}$. In case of organic-inorganic hybrids doped with silver nanoparticles, the surface plasmon band intensity increase with increasing in silver concentration. The shift toward much higher wave number is due to the increase of particles size and of the amount of silver nanoparticles in the composite film.

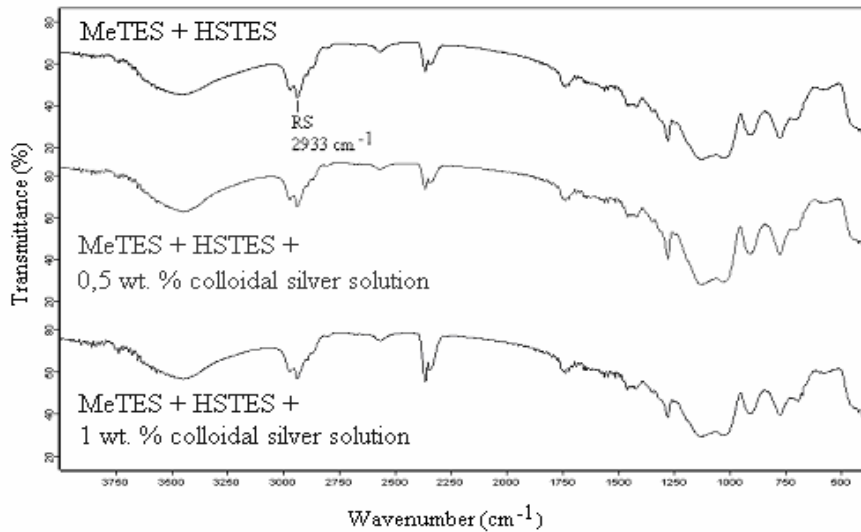


Fig. 7 – FT-IR spectra for MeTES+HSTMS – based hybrids, doped with different colloidal silver solutions.

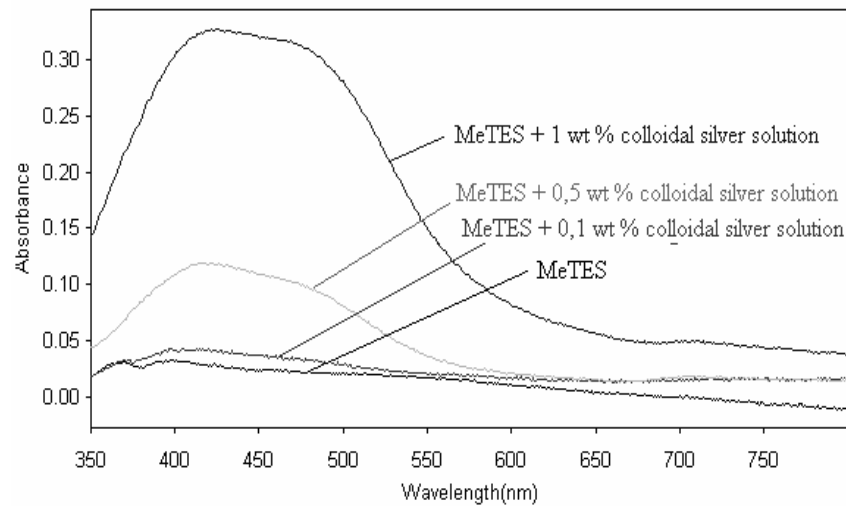


Fig. 8 – UV-VIS spectra for MeTES – based hybrids, doped with different colloidal silver solutions.

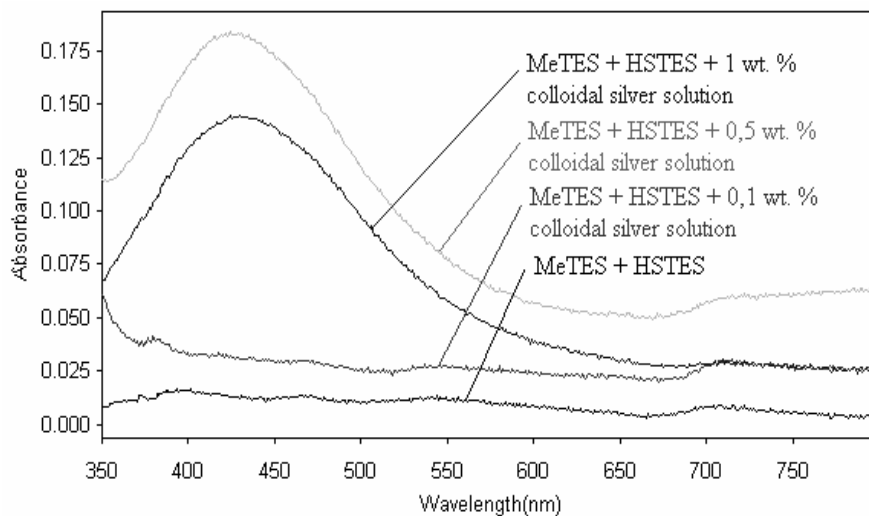


Fig. 9 – UV-VIS spectra for MeTES+HSTMS – based hybrids, doped with different colloidal silver solutions.

For example, the UV-VIS spectra of the hybrids with MeTES and also of the hybrids with MeTES and HSTMS, doped with Rhodamine B and colloidal silver (at different concentrations) are presented in figures 10 and 11.

To show the effect on the absorption domains for metal plasmons and for dyes as well, the UV-VIS spectra of the hybrids (prepared as in table 1) were registered. The Rhodamine B dimers amount is lower in organic-inorganic hybrid materials than in ethanol-water solutions. For this reason, in figures 13, 15, 17 and 19 we present just absorbance for monomers.

In order to compare the differences between spectral data, the maximum wavelength (λ_{\max}) of the dyes were measured and represented.

The wavelength modifications for the emission peak of the silver and of the different dyes used in case of hybrids (with MeTES or with MeTES and HSTMS), are showed in the diagrams 12-19, for different concentrations of colloidal silver. It is obvious that HSTMS, which affects the hybrids morphology, contributes also to the incorporation of the silver nanoparticles and modifies the spectral properties of the hybrids for silver and for dyes absorption area.

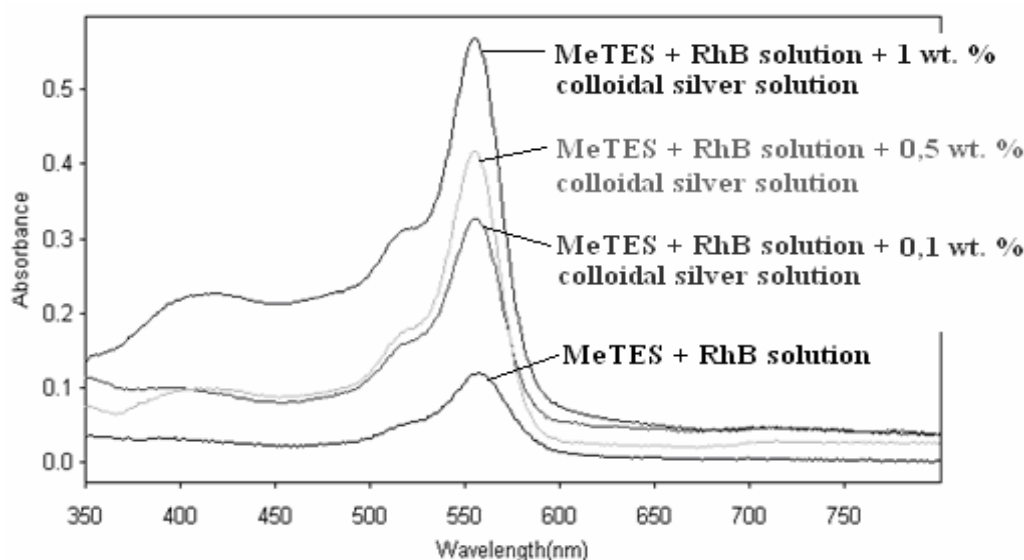


Fig. 10 – UV-VIS spectra of MeTES – based hybrids, doped with Rhodamine B (RhB) at different colloidal silver concentrations.

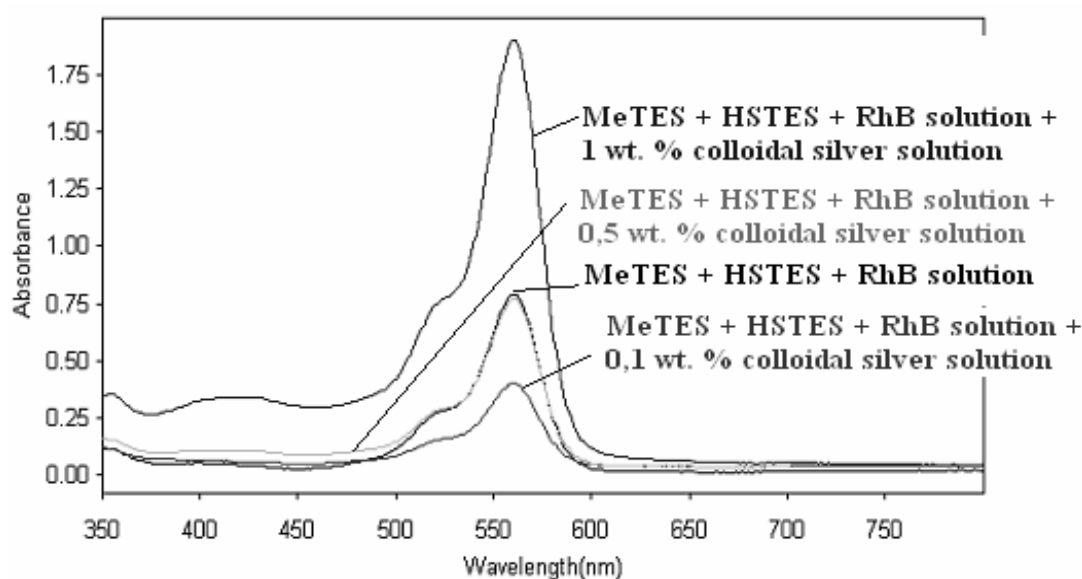


Fig. 11 – UV-VIS spectra of MeTES+HSTMS – based hybrids, doped with Rhodamine B (RhB) at different colloidal silver concentrations.

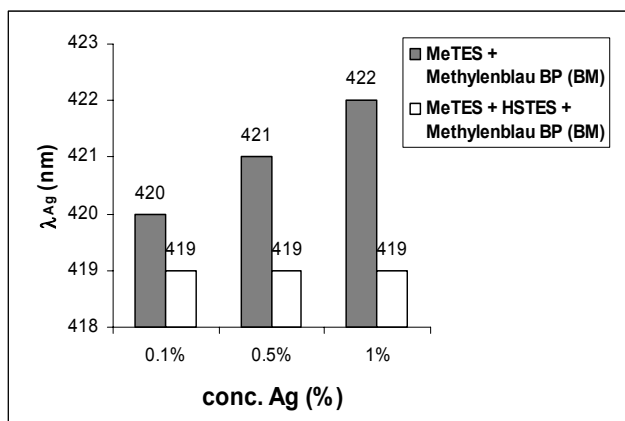


Fig. 12 – The wavelength changing of of the silver emission peak for MeTES and MeTES+HSTMS – based hybrids, doped with Methyleneblau BP (BM), as function of silver concentration.

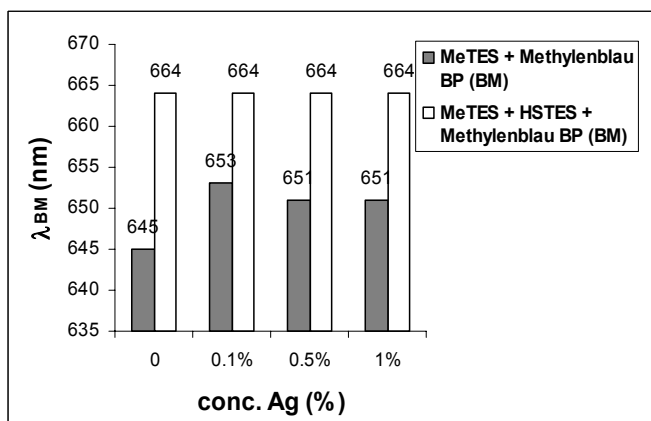


Fig. 13 – The wavelength changing of Methyleneblau BP (BM) emission peak for MeTES and MeTES+HSTMS – based hybrids, doped with BM, as function of silver concentration.

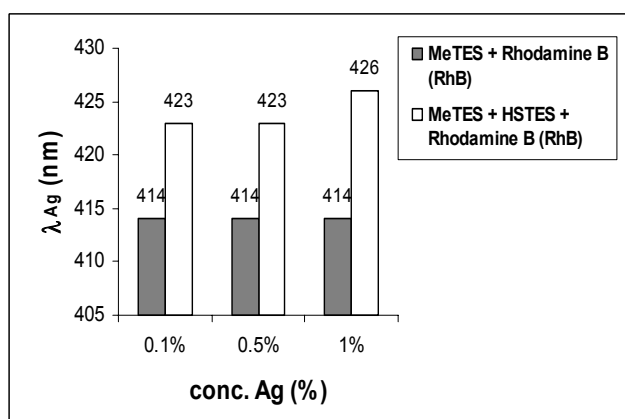


Fig. 14 – The wavelength changing of silver emission peak for MeTES and MeTES+HSTMS – based hybrids, doped with Rhodamine B (RhB), as function of silver concentration.

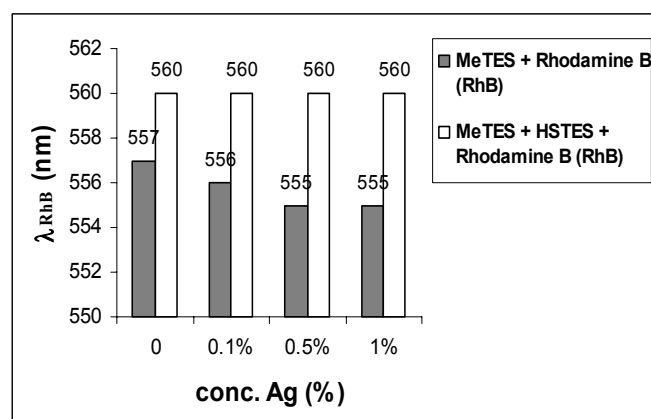


Fig. 15 – The wavelength changing of Rhodamine B (RhB) emission peak for MeTES and MeTES+HSTMS – based hybrids, doped with RB, as function of silver concentration.

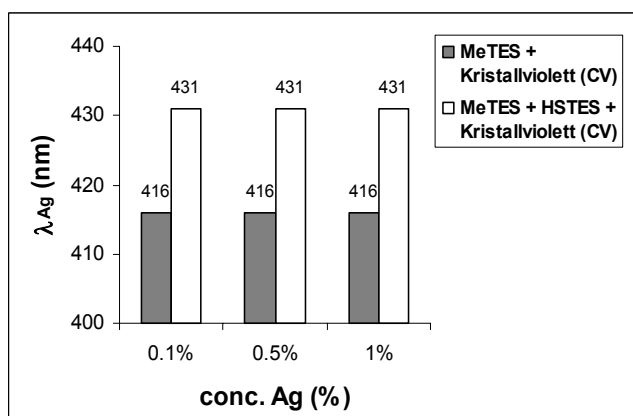


Fig. 16 – The wavelength changing of silver emission peak for MeTES and MeTES+HSTMS – based hybrids, doped with Kristallviolett (CV), as function of silver concentration.

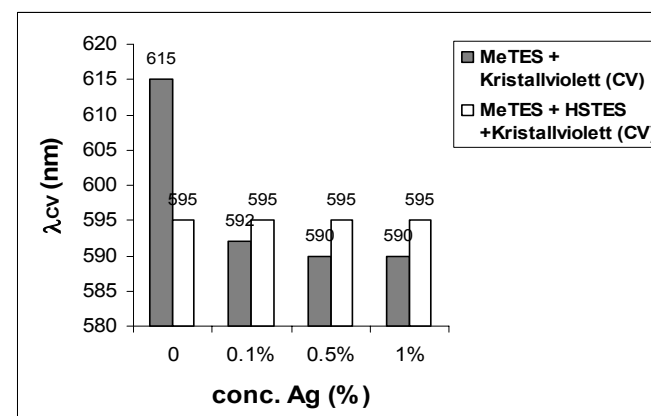


Fig. 17 – The wavelength changing of Kristallviolett (CV) emission peak for MeTES and MeTES+HSTMS – based hybrids, doped with CV, as function of silver concentration.

According to previous reviews, an increasing of the maximum wavelength (λ_{\max}) was observed in many cases for silver and dyes at hybrids with MeTES and HSTMS.^{2, 5, 11, 29} The thio group from

HSTMS interacts with silver particles surface and causes a red shift (increase λ_{\max}) of the absorption maximum.¹⁵ Exceptions are the Methyleneblau BP – doped hybrids (figure 14) because the dye contains

in its structure sulfur atom. The sulfur atom can interact itself with the metallic nanoparticles. Due to this interaction, which compete with HSTMS one, a shift of the maximum wavelength to lower values is produced. In all cases, for the maximum absorption of the dyes, an increasing of λ_{\max} for

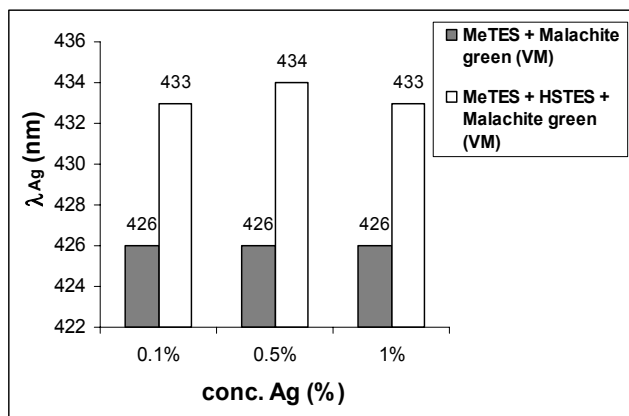


Fig. 18 – The wavelength changing of silver emission peak for MeTES and MeTES+HSTMS – based hybrids, doped with Malachite green (VM), as function of silver concentration.

This decrease of nanoparticles dimensions generates the increase of the interface surface with the dyes. These dyes can interact in a higher amount with silica because they contain acidic groups. The higher polarity of the silica causes the modification toward higher values of λ_{\max} like in the case other hybrids.^{2,3}

According to our knowledge, these effects induced by the change of the nanodomains polarity were not showed yet. Similarly, the absorption area for silver nanoparticles as well as for the dyes is changing with the modification of the hybrids composition.

The increase of the absorbance signal from 400 nm, as well as the ones specific to each dye (see figure 10), with the increase of the silver concentration, is another very important observation. This is a proof that both silver nanoparticles and dye have a modified dispersivity in the hybrid films. Our conclusions are based on the modification of absorption signal and of λ_{\max} for Rhodamine B solution in ethanol/water mixtures (figures 1-4). The decrease of λ_{\max} value is due to the decrease of the medium polarity, starting from water to alcohol. This is a very complex process. The nonlinear variation of the λ_{\max} in ethanol/water mixtures is a proof of different associated forms by hydrophobic

hybrids with MeTES and HSTMS is noticed. The modification of the MeTES+HSTMS – based hybrids morphology was demonstrated.¹²⁻¹⁴ In the case of thio derivate, the decrease of polarity and also dimensions of the nanodomains, which forms the hybrids, was observed.

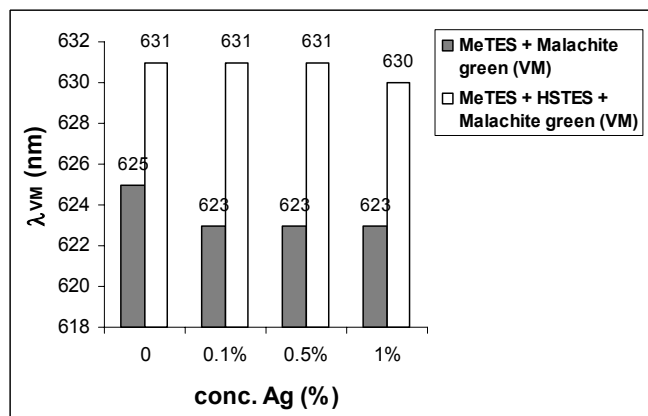


Fig. 19 – The wavelength changing of Malachite green (VM) emission peak for MeTES and MeTES+HSTMS – based hybrids, doped with VM, as function of silver concentration.

demixing of the ethyl chains from the organic solvent.^{30, 31} These phenomena were also confirmed by fluorescence, refractometry and conductometry studies.³¹

The nonlinear modification of the absorbance at a well established concentration of Rhodamine B, but at a different type of nanostructuration (variable ethanol/water ratio), showed, although the dye is soluble both in water and ethanol, that:

Mono-domains achieved at $x_{\text{ethanol}} < 0.166$ (x_{ethanol} = the molar fraction of ethanol) are o/w (oil/water) type microemulsion;

At $x_{\text{ethanol}} > 0.166$ are bicontinuous type microemulsion;

w/o ratio affects the dye's dispersion.³¹

The morphology of the MeTES hybrid films doped with 0.1 wt. % colloidal silver solution was evaluated by SEM. The surface of the hybrids was found to be homogenous, without any obvious phase separations (figure 20).

For MeTES+HSTMS based hybrid film, doped with 0.1 wt. % colloidal silver solution, some associations could be seen on its surface, but without any obvious phase separation (see figure 21).

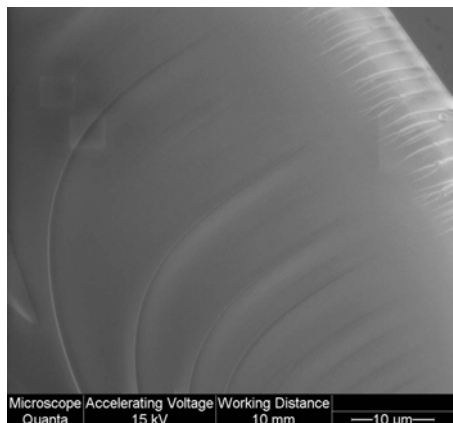


Fig. 20 – SEM picture of the surface morphology of MeTES based hybrid, doped with 0.1 wt. % colloidal silver solution.

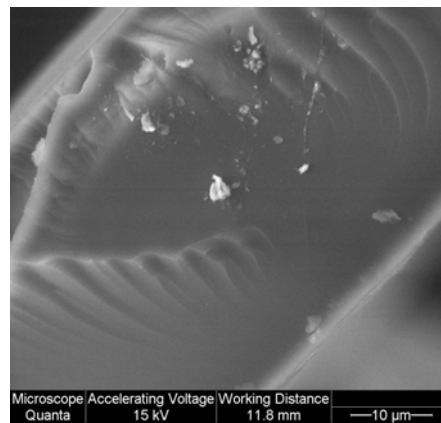


Fig. 21 – SEM picture of the surface morphology of MeTES+HSTMS based hybrid, doped with 0.1 wt. % colloidal silver solution.

EXPERIMENTAL

Materials

Colloidal silver powder from ARGENOL, methyltriethoxysilane (MeTES) and 3-(trimethoxysilyl)-1-propanthiol (HSTMS) from Merck Schuchard, tetraisopropyl orthotitanate (TIP) and maleic anhydride (MA) from Fluka AG, Methylenblau BP (BM) from Loba Feinchemie, Rhodamine B (RB) from Gliwice Polska, Kristallviolett (CV) from Loba Feinchemie, Malachite green (VM) from Kordon Corp.

Film preparation

Hybrid films were prepared by the sol-gel method, in two-steps, because tetraisopropyl orthotitanate (TIP) hydrolyzes at

a much higher rate than the MeTES. First, MeTES was prehydrolyzed, with and without HSTMS, in acidic conditions with ethanol (5 ml) and water (0.56 ml), or with ethanol, colloidal silver solutions at three different concentrations (0.1%, 0.5% and 1%) for 1h, under continuous stirring. As a second step, the TIP and maleic anhydride (MA) were added to the solution, together with the second portion of water (1.2 ml) or colloidal silver solution and mixed for another hour. The amounts of materials used are summarized in Table 1. From each final solution, equal ratio were taken and mixed with different dyes (Methylenblau BP (BM), Rhodamine B (RhB), Kristallviolett (CV), Malachite green (VM)), with concentration $\sim 10^{-6}$ mol/l and stirred for 15 min. Hybrids films were deposited on glass slides by dip-coating and then the slides were dried at room temperature (25°C).

Table 1

The amounts of used materials

MeTES (ml)	HSTMS (ml)	EtOH (ml)	H ₂ O (ml)	Ag (ml/%)	TIP (ml)	MA (g)
9	-	5	1.76	-	0.8	0.152
9	-	5	-	1.76 (0.1%)	0.8	0.152
9	-	5	-	1.76 (0.5%)	0.8	0.152
9	-	5	-	1.76 (1%)	0.8	0.152
4.5	4.2	5	1.76	-	0.8	0.152
4.5	4.2	5	-	1.76 (0.1%)	0.8	0.152
4.5	4.2	5	-	1.76 (0.5%)	0.8	0.152
4.5	4.2	5	-	1.76 (1%)	0.8	0.152

Techniques

The colloidal silver powder prepared at three different concentrations (0.1%, 0.5% and 1%) was analyzed by dynamic light scattering (DLS) (Nano-ZS from Malvern). UV-VIS absorption spectra of the hybrid films were acquired in the range of 350-800 nm using an UV-VIS spectrophotometer (Nicolet Evolution 500 from Thermo Electron Corporation). FT-IR spectra, in the range 400-4000 cm^{-1} using a Fourier transforms infrared spectrometer (Tensor 37 from Bruker) were measured in transmission mode using potassium bromide (KBr)-based pellets. The surface of the hybrid films doped with colloidal silver was visualized by scanning electron microscopy (SEM) (FEI QUANTA 200).

CONCLUSIONS

We have demonstrated that UV-VIS spectra showed the modifications of colloidal silver and dyes absorption domain, depending on silver nanoparticles concentration and on hybrids polarity. The dye adsorption of the silver nanoparticles induces the modification of spectral characteristics in case of Methylenblau BP (BM), colorant that is different from the other dyes.

From evaluation of FT-IR spectra of the colloidal silver doped films were not observed

significant modifications, at the used concentrations of colloidal silver.

Adding of HSTMS, which affects the hybrids morphology, contributes to the incorporation of the silver nanoparticles and changes the internal composition of hybrid films.

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