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INCORPORATION OF AU AND AG NANOSTRUCTURES INSIDE SiO_2

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ABSTRACT

Incorporation of Au° inside SiO_2 was achieved by a solid-state method from the pyrolysis of the composites (Chitosan)•$(AuCl_3)_n$•$(SiO_2)_m$ and (PS-co-4-PVP)•$(AuCl_3)_n$•$(SiO_2)_m$ Similarly, the incorporation of Ag° inside SiO_2 it was made from thermal treatment of the composites (Chitosan)•$(AgNO_3)_n$•$(SiO_2)_m$ and (PS-co-4-PVP)•$(AgNO_3)_n$•$(SiO_2)_m$. The nature of the polymer controls the particle size for the Au/SiO_2 composite, while that for the Ag/SiO_2 both, polymer Chitosan and PS-co-4-PVP, produces similar particle size. In the case of the composite Ag/SiO_2 the particle size as small as 5 nm were obtained.

The 1:1 or 1:5 metal/polymer ratios, as well as the nature of the polymer in the macromolecular precursors (Chitosan)•$(AuCl_3)_n$•$(SiO_2)_m$ and (PS-co-4-PVP)•$(AuCl_3)_n$•$(SiO_2)_m$ influences the dispersion of the Au° nanostructures inside SiO_2 matrix. The results are compared with those previously obtained for bimetallic composites Au/Ag//SiO_2. A formation mechanism of the Au°/SiO_2 and Ag°/SiO_2 composites involving the combustion of the organic matter and the growth of the Au° and Ag° nanoparticles inside the holes, generated from the combustion process, is proposed.

Keywords: Gold nanoparticles, Silver nanoparticles, silica, composites.

1.- INTRODUCTION

Among the several practical applications of the metallic and metal oxides nanoparticles and nanostructured materials, are those in catalysis[1,2]. In this field, the heterogeneous catalyst is one of the most important and most widely used in industrial processes. Is well known that the incorporation of these metal oxides on the inert supports materials, with high surface areas to form composites materials, could help to prevent their aggregations and improvement their reactivity and stability[3,4]. Specifically the nanocomposites Au°/SiO_2 are an important catalyst for several oxidation processes[5,6] . Since the finding by Haruta et al[7,8] of the high performance low temperature oxidation of CO by Au °/SiO_2, several other oxidation processes, using this nanocomposites have been reported. Because of the usual solution method to prepare this catalyst composite, presents some problems due to the difficulty of depositing the Au° nanoparticles inside SiO_2 the adequate preparation of Au°/SiO_2, is a constant challenge[9,10] Then, the new easily, fast and direct methods for to prepare nanoparticles and nanostructures anchored to a solid supporting is a constant challenge. The solution ways to synthesize this type of system, they have the difficulty that, on carry the nanoparticles, from solution to solid-state anchored over a solid support, they undergoes usually agglomeration with loss of the nanoscale properties[11-14].

On the other hand, the interest of the Ag°/SiO_2 composites mainly arises from the antimicrobial properties[15] of Ag° as well as from their catalysis[16] and their electronic devices practical applications[17]. These interesting properties of the Ag° nanoparticles are they are altered by the uncontrollable release of Ag^+ by oxidation on O_2 which cause toxicity in the antimicrobial properties, oxidation to Ag^+ in the high temperature catalyst applications decreasing the catalytic efficiency and loss of the plasmon resonance, important in the electronic applications , also by the oxidation of Ag° to Ag^+. All these disadvantage of the use of Ag° in practical applications can be solved by their encapsulation in SiO_2[18-21.] Several solution methods to prepare Ag°/SiO_2 including the most usual, the impregnation of previously formed SiO_2 with some Ag^+ salt afford in some cases partial formation of Ag_2O/SiO_2[22]. Here we present a route where phase pure Ag°/SiO_2 is obtained and further is general for the synthesis of both Au°/SiO_2 and Ag°/SiO_2. In contrast with the here reported method where, the pure phase Ag° nanoparticles inside SiO_2 was observed, in ours previous reports, the thermal treatment the containing Ag+ $[(O_3SCF_3)Ag(PPh_3)(HOC_5H_4N)][SiO_2]n$ precursors affords Ag_2O inside SiO_2 nanoparticles[22].

Previously we have reported a versatile and reliable solid-state method to prepare metallic and metal oxides nanostructures materials[22-26] and their incorporation in SiO_2 matrices[27,28]. The method consists in the pyrolysis of the macromolecular precursors (Chitosan)•$(MLn)_n$•(SiO_2)m and (PS-co-4-PVP)•$(MLn)_n$.$(SiO_2)_m$ where the precursors (Chitosan)•$(MLn)_m$ and (PS-co-4-PVP)•$(MLn)_m$ are generated according previous reports [22-26] .Now, we use this approach to prepare Au° and Ag° inside SiO_2 to give Au/SiO_2 and Ag/SiO_2 composites founding that the dispersion of the metal noble nanoparticles into the silica matrix can be controlled by the 1:1 or 1:5 metal/polymer ratio, as well as, by the nature of the polymer. The results are compared with those previously obtained[27] for bimetallic composites Au/Ag//SiO_2. A preliminary work showing some of these result have been reported[27].

2.- EXPERIMENTAL

$AuCl_3$ and $Ag(NO_3)$, PSP-co-4-PVP, Chitosan, TEOS (tetraethoxysilane) and acetic acid were purchased from Aldrich and used as received. All the reactions were performed using CH_2Cl_2 as solvent and nanopure water.

2.1.- Precursors Synthesis: Chitosan•(MLn)n MLn=$AuCl_3$ and $Ag(NO_3)$

In a typical synthesis [22-26], the respective metallic salts $AuCl_3$ and $Ag(NO_3)$ were added in a Schlenk tube using CH_2Cl_2 as solvent under magnetic stirring and then the respective Chitosan amount was added according to the 1:1 (**1**),**(5)** or 1:5 (**2**), **(6)** respectively for Au and Ag molar ratio (compound numeration according Table 1).

	Precursor	**Metal/ polymer ratio**	**g. of Chitosan or PS-co-4-PVP**	**g. of metallic salt**
1.-	(Chitosan•$(AuCl_3)_n$•$(SiO_2)_n$	1:1	0.20	0.35
2.-	(Chitosan•$(AuCl_3)_n$•$(SiO_2)_n$	1:5	2.31	0.40
3.-	(PS-co-4-VP)•$(AuCl_3)$n•$(SiO_2)_n$	1:1	0.20	0.35
4.-	(PS-co-4-PVP)•$(AuCl_3)_n$•$(SiO_2)_n$	1:5	0.78	0.45
5.-	(Chitosan•$(AgNO_3)_n$•$(SiO_2)_n$	1:1	0.41	0.40
6.-	(Chitosan•$(AgNO_3)_n$•$(SiO_2)_n$	1:5	1.55	0.30
7.-	(PS-co-4-PVP)•$(AgNO_3)_n$•$(SiO_2)_n$	1:1	0.23	0.37
8.-	(PS-co-4-PVP)•$(AgNO_3)_n$•$(SiO_2)_n$	1:5	1.33	0.43

Table 1. Experimental Details of the synthesis of the precursors 1-6

After 7 days, the supernatant solution (if the solid decanted) was extracted with a syringe and the solid was dried under reduced pressure, resulting a yellow-red solid. See Table 1.

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2.3.- SiO_2

SiO_2 was prepared according a literature method [27, 28]. Briefly, TEOS, ethanol, acetic acid in molar ratios 1:4:4 and water nanopure were stirring for 3 days. The wet gels were further dried at 100 °C under reduced pressure in a vacuum furnace. Finally, the solids were calcined at 800 °C for 2 h.

2.4.- $(Chitosan)\bullet(MLn)_n\bullet(SiO_2)_m$ and $(PS\text{-}co\text{-}4\text{-}PVP)\bullet(MLn)_n\bullet(SiO_2)_m$ precursors

The $(Chitosan)\bullet(AgNO_3)_n\bullet(SiO_2)_m$ and $(PS\text{-}co\text{-}4\text{-}PVP)\bullet(AgNO_3)_n\bullet(SiO_2)_m$ were prepared by simple solid-state mixture of the as prepared $(Chitosan)\bullet(MLn)_n$ and $(PS\text{-}co\text{-}4\text{-}PVP)\bullet(MLn)_m$ and SiO_2 and subsequent grinding of the solid mixture in a 1:10 molar ratio.

2.5.- Pyrolysis

The pyrolysis experiments were conducted by pouring a weighed portion (0.05–0.15 g) of the respective $(Chitosan)\bullet(AgNO_3)_n\bullet(SiO_2)_m$ and $(PS\text{-}co\text{-}4\text{-}PVP)\bullet(AgNO_3)_n\bullet(SiO_2)_m$ precursors into aluminum oxide boats that were placed in a furnace (Labtech.LEF-10 oven) under a flow of air, heating from 25°C to upper temperature limits of 300°C, and then to 800 °C, followed by annealing for 2-4 h and at rates of 10 °C min-1 in each case.

2.6.- Characterization of the pyrolytic products

Solid pyrolytic samples were characterized by powder x-Ray diffraction (XRD) and scanning electron microscopy (SEM). SEM images were acquired with a JSM-6380LV, JEOL Ltda. microscope, with an acceleration potential of 20 keV. Energy dispersive X-ray analysis (EDS) was performed on a NORAN Instrument micro-probe attached to a JEOL 5410 scanning electron microscope. High-Resolution Transmission Electron Microscopy (HR-TEM) was performed using a JEOL 2000FX TEM microscope at 200 kV to characterize the average particle size, distribution and elemental and crystal composition. X-ray diffraction (XRD) was conducted at room temperature on a Siemens D-5000 diffractometer with θ-2θ geometry. The XRD data was collected using Cu-Kα radiation (40 kV, 30 mA). FTIR measurements were performed on a Perkin Elmer FTIR spectrophotometer model Spectrum BXII. UV-vis spectra were performed on a Shimadzu UV 2450 spectrophotometer.

3.- RESULT AND DISCUSSION

A pictorial drawing showing the methodology used for the preparation of the composites Au/SO_2 and $Ag//SiO_2$ is displayed in Figure 1.

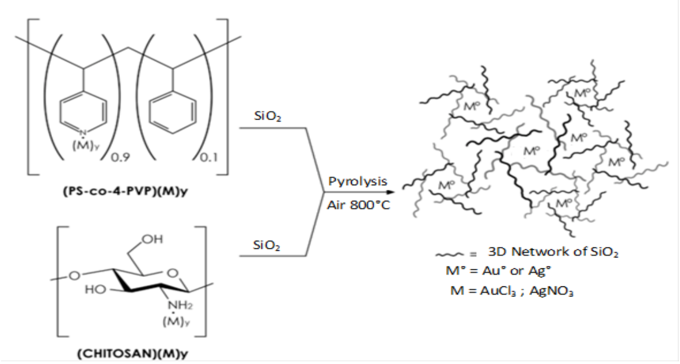

Figure 1. Schematic representation of preparation of Au/SO_2 and $Ag//SiO_2$ composites.

The macromolecular complexes $(PS\text{-}co\text{-}4\text{-}PVP)\bullet(AuCl_3)_n$ and $(Chitosan\bullet(AuCl_3)_n$ prepared as previously described (see experimental part and ref. 22-26).and the SiO_2 (prepared by sol-gel method see experiemental part and ref. 27, 28) were mixture in solid state in a crucible and pyrolyzed under air at 800 °C. The composites were first characterized be powder XRD- ray diffraction. Figure 2 shows as a representative, the diffraction pattern of Au/SO_2, from the precursor $(PS\text{-}co\text{-}4\text{-}PVP)\bullet(AuCl_3)_n\bullet(SiO_2)_n$, as well as from $(Chitosan\bullet(AuCl_3)_n\bullet(SiO_2)_n$ in a pure phase. Clearly the (111), (200), (220) and (311) main diffraction planes of Cubic Au are observed. A broad direction peak at 2θ= 23° is assigned to amorphous silica. Thus, these diffraction patterns are similar to that of reported for Au/SO_2 composites using a several solution and another miscellaneous methods[29].

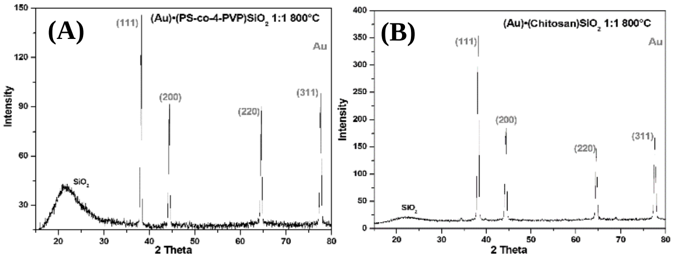

Figure 2. XRD diffraction pattern of the composite Au/SiO_2 from the $(PS\text{-}co\text{-}4\text{-}PVP)\bullet(AuCl_3)_n\bullet(SiO_2)_m$, 1:1 precursor (A) and from $(Chitosan\bullet(AuCl_3)_n\bullet(SiO_2)_m$ 1:1 (B).

Similar XRD pattern was found for the Au/SO_2 prepared from the precursors $(Chitosan\bullet(AuCl_3)_n\bullet(SiO_2)_m$ see figure 2 (B).

On the other hand the XRD patterns diffraction for the composites $Ag//SiO_2$ from both polymer precursors , see figure 3 (A) and (B), exhibits a similar peaks patterns to that of Au/SiO_2 due to both Au and Ag they have a similar unitary cell[27]. Both XRD diffraction are in agreement with whose reported for another $Ag//SiO_2$ composite prepared from solution[20,21].

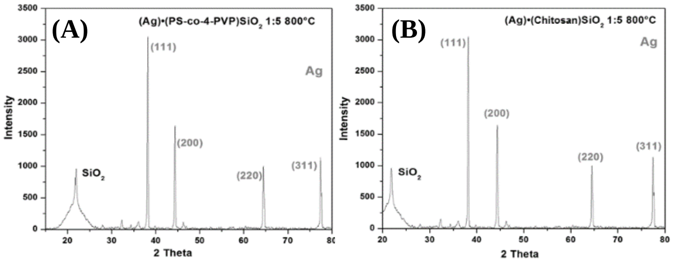

Figure 3. XRD diffraction pattern of the composite Ag/SO_2 from the $(PS\text{-}co\text{-}4\text{-}PVP)\bullet(AgNO_3)_n\bullet(SiO_2)_m$, 1:1 precursor (A) and from $(Chitosan\bullet(AgNO_3)_n\bullet(SiO_2)_m$ 1:5 (B).

Notwithstanding the above the presence of Au and Ag inside the matrix SiO_2 was corroborate by their SEM-EDS analysis as is shown in figure 4. The presence of Si, O and Au for the composite Au/SiO_2 ,figure 4 (A) and (B) and the presence of Si, O and Ag for the composite Ag/SiO_2 , figure 4 (C) and (D) was clearly confirmed from these images. Thus the morphology observed shows somewhat irregular shapes with exception in figure 4 (D) where some spheres of SiO_2 surrounded of some Au nanoparticles.

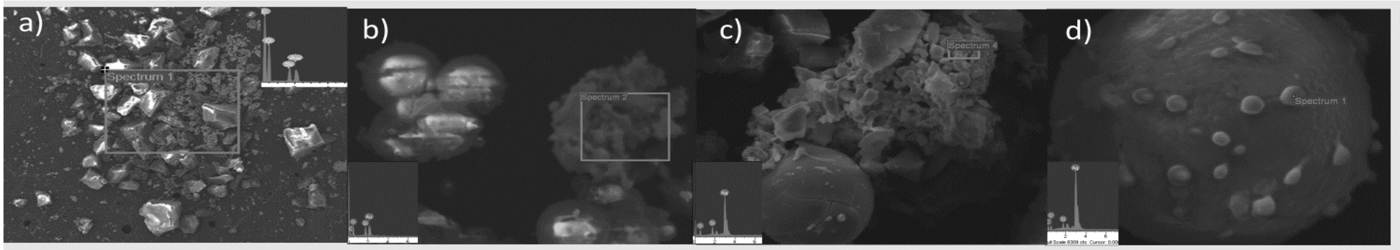

Figure 4. SEM image together with their EDS analysis (inset) for of the composite Au/SO_2 from the $(PS\text{-}co\text{-}4\text{-}PVP)\bullet(AuCl_3)_n\bullet(SiO_2)_m$, 1:1 precursor (A) and from $(Chitosan\bullet(AuCl_3)_n\bullet(SiO_2)_m$ 1:1 (B) as well as for composite Ag/SO_2 from the $(PS\text{-}co\text{-}4\text{-}PVP)\bullet(AgNO_3)_n\bullet(SiO_2)_m$, 1:5 precursor (C) and from $(Chitosan\bullet(AgNO_3)_n\bullet(SiO_2)_m$ 1:5 (D).

The TEM images, see figure 5, shows the TEM image for the Au/SiO_2 and Ag/SiO_2 obtained from the precursors with both polymer Chitosan and PS-co-4-PVP. For Au/SiO_2 the TEM images shows the Au nanoparticles well dispersed inside SiO_2 for the nanocomposite prepared from (Chitosan•$(AuCl_3)_n$•$(SiO_2)_m$ precursor with average size of 5.7 nm (see histogram inside) but with some agglomerates nanoparticles into SiO_2 composite from the (PS-co-4-PVP)•$(AuCl_3)_n$•$(SiO_2)_m$, with average size of 108 nm (see histogram inside figure).

Similar TEM images were obtained for Au/SiO_2 composites obtained by other methods [9.10].

On the other hand well dispersed Ag nanoparticles inside SiO_2 where observed for the Ag/SiO_2 composites obtained from (Chitosan•$(AgNO_3)_n$•$(SiO_2)_m$ figure 5d and (PS-co-4-PVP)•$(AgNO_3)_n$•$(SiO_2)_m$,, figure 5c, with particle size 5 nm and 6 nm respectively obtained from the respective inset histograms. Similar TEM images were obtained for Ag/SiO_2 composites prepared by other methods. [21,30].

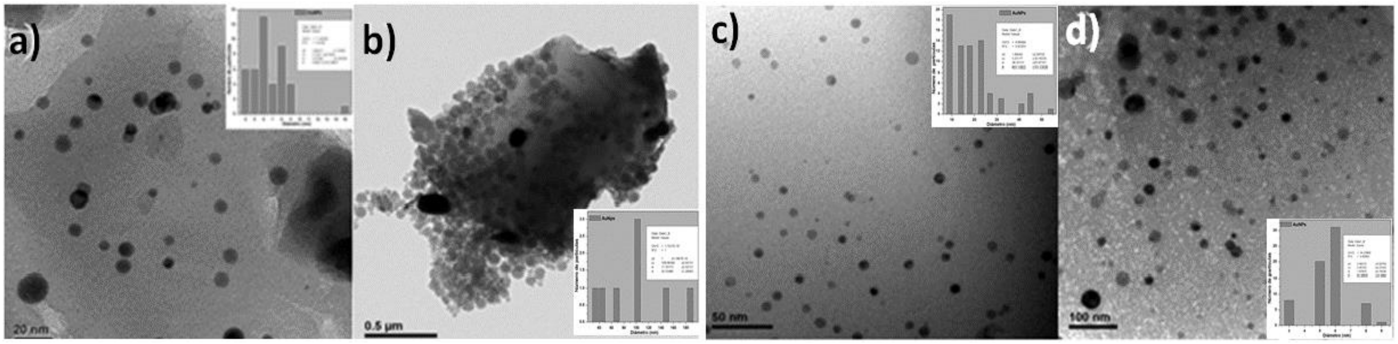

Figure 5. TEM image with their histogram (inset) for of the composite Au/SO_2 from the (PS-co-4-PVP)•$(AuCl_3)_n$•$(SiO_2)_m$, 1:1 precursor (A) and from (Chitosan•$(AuCl_3)_n$•$(SiO_2)_m$ 1:1 (B) as well as for composite Ag/SO_2 from the (PS-co-4-PVP)•$(AgNO_3)_n$•$(SiO_2)_m$, 1:5 precursor (C) and from (Chitosan•$(AgNO_3)_n$•$(SiO_2)_m$ 1:5 (D).

Some most detailed features are observed by HRTEM. For instance from figure 6 two Au overlapping nanoparticles and other two isolates both with size near to 5 nm as observed in the histogram from the TEM , se figure 6 a,b,c.These were obtained from the precursor (PS-co-4-PVP)•$(AuCl_3)_n$•$(SiO_2)_m$. From Au nanoparticles from the Chitosan•$(AuCl_3)n$•$(SiO_2)_m$ precursor most rather large nanoparticles were observed as is observed from figure 5c,f. Interplanar distances corresponding to the plane typical of Au were observed as is showed in figure 5 e, f.

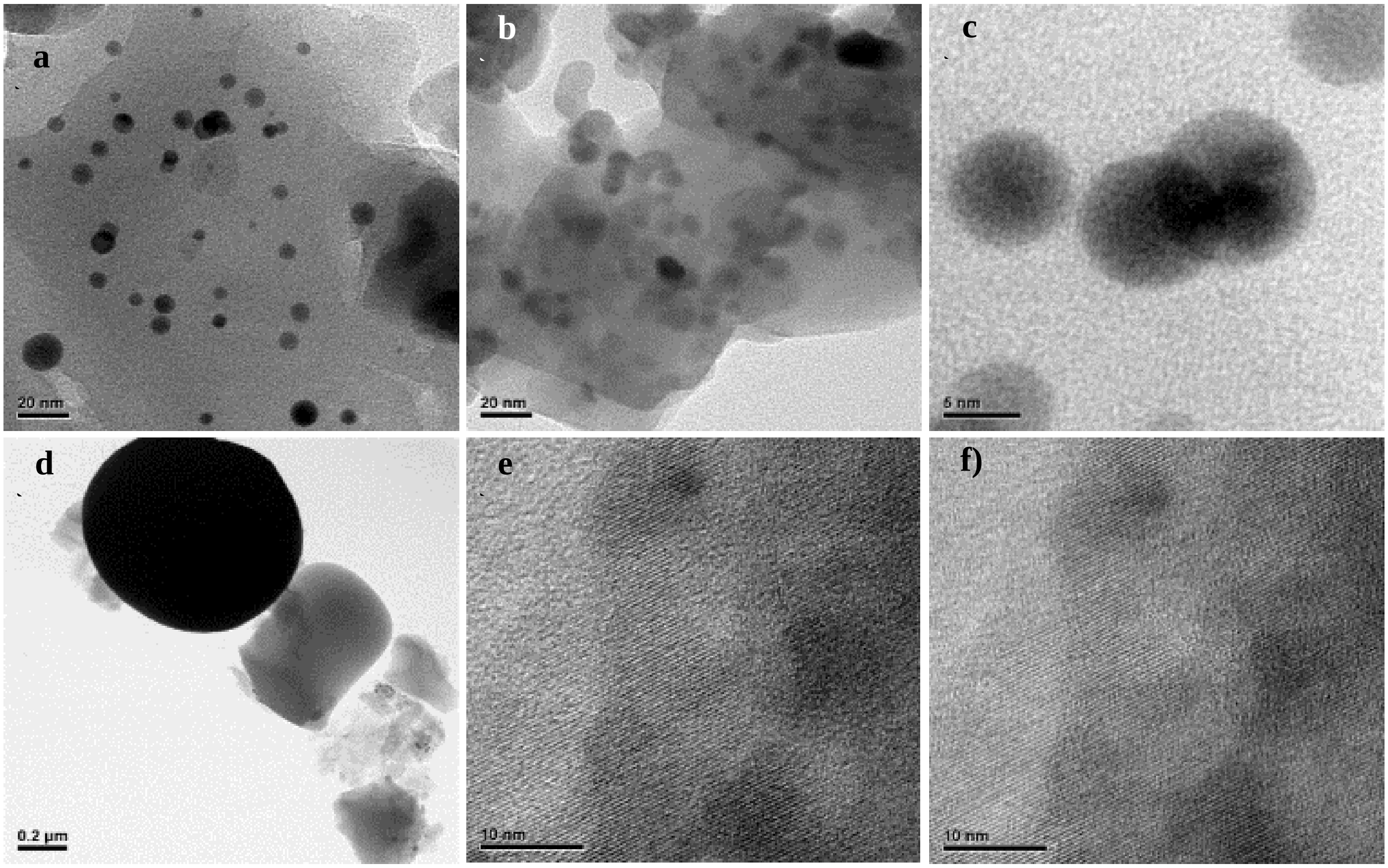

Figure 6. HRTEM images of Au nanoparticles from (PS-co-4-PVP)•$(AuCl_3)_n$•$(SiO_2)_m$ (a), (b) ,(c) and from Chitosan•$(AuCl_3)_n$•$(SiO_2)_m$ (d), (e) and (f).

Most detailed information of the dispersion of the Au nanoparticles inside SiO_2 was obtained from SEM-EDS mapping by element. Figure 7 shows Au nanoparticles well dispersed inside SiO_2 for the nanocomposite prepared from 1:1 and 1:5, as well as from (Chitosan•$(AuCl_3)_n$•$(SiO_2)_m$ 1:1and 1:5 precursor.

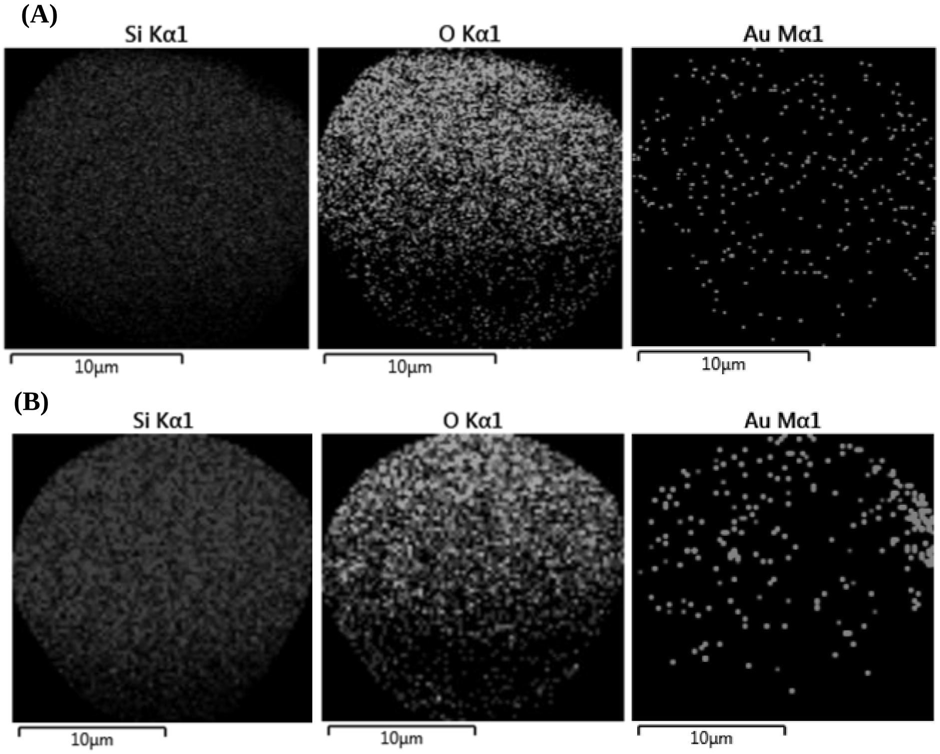

Figure 7. EDS mapping by elements of the Au/SiO_2 nanocomposite from the precursor (Chitosan•$(AuCl_3)_n$•$(SiO_2)_m$ in 1:1 (A) and 1:5 (B) molar metal polymer ratio. Similar well dispersed Au into silica was observed for the composite Au/SiO_2 prepared from precursors 1:5 (Chitosan•$(AuCl_3)_n$•$(SiO_2)_m$ see figure 6 (B) but with minor content of Au nanoparticles dispersed into silica.

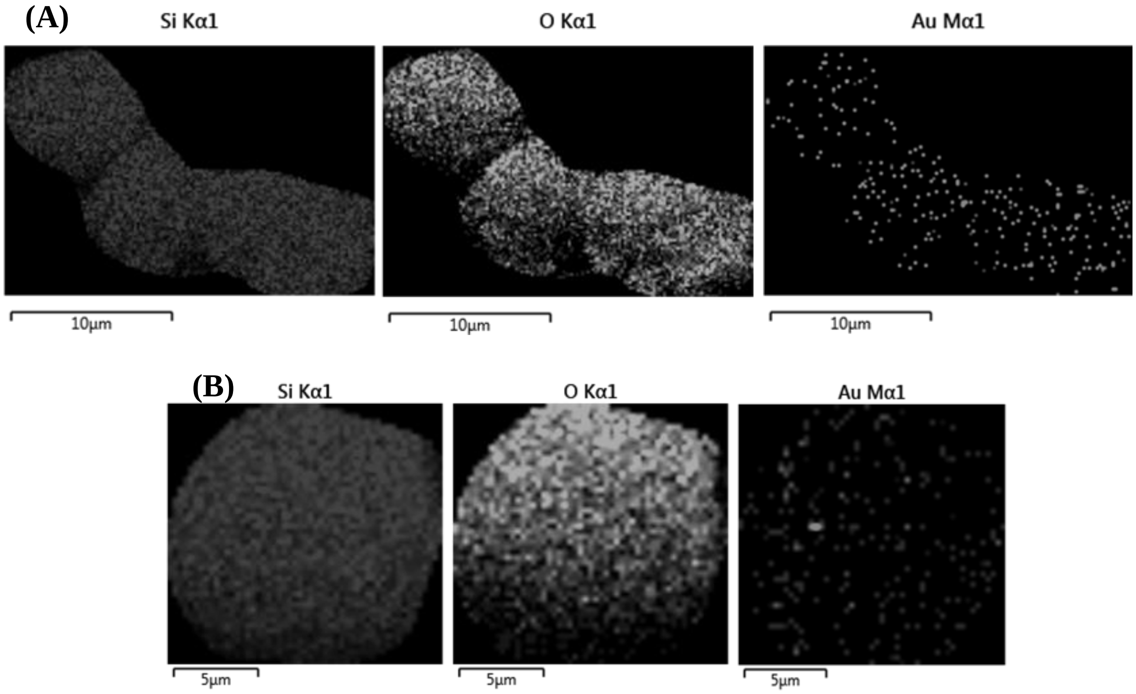

Figure 8. EDS mapping by elements of the Au/SiO_2 nanocomposite from the precursor 1:1 (A) and 1:5 (B) (PS-co-4-PVP)•$(AuCl_3)_n$•$(SiO_2)_m$.

Similar results were obtained from both, 1:1 and 1:5, (PS-co-4-PVP)•$(AuCl_3)_n$•$(SiO_2)_m$ precursors, although in this later case with less amount of Au nanoparticles incorporated into Silica.

For these systems the macromolecular complexes 1:5 metal/polymer ratio induce, a most well dispersed distribution of the Au$^{\circ}$ nanoparticles inside silica than the 1:1 metal/polymer ratio precursor. Using a similar solid-state method, the composites Au/Ag//SiO_2 from the pyrolysis of the macromolecular precursors PSP-4-PVP•$(AuCl_3/AgSO_3CF_3)_n$•SiO_2 and Chitosan •$(AuCl_3/AgSO_3CF_3)$n•SiO_2 both in 1:1, and 1:5 molar ratios have been obtained[27] **.** For this system, a similar tendency was observed.

In basis of previous studies about the formation mechanism of M° and metal oxides nanoparticles using the solid state method, and macromolecular metal-polymer complexes as precursors[31] a tentative formation of the formation of the Au// SiO_2 and Ag//SiO_2 nanocomposites can be proposed.

The first step on heating the macromolecular metal-polymer complexes involves the formation of a 3D network[32] to produce a thermal stable matrix, shown in Fig. 9. In our system, the first heating step likely involves a cross-linking of the Chitosan and PSP-4-PVP polymer precursors to give a 3D matrix containing ●-O-M-O-●, ●-H_2N-M-NH_2-● as well as ●-O-M- NH_2-● links M= Au^{3+} and Ag^{+} in the case of Chitosan and ●-C_5H_4N-M-N C_5H_4-● M= Au^{3+} and Ag^{+} in the case of PSP-4-PVP with --● the respective polymer backbone. This step precludes a physical evaporation of the respective polymer on heating. The following steps involves the initiation of the organic carbonization, where in presence of air and of incomplete combustion can produce some CO which reduce the Au^{3+} and Ag^{+} to Au° and Ag° [33] respectively. Following this, holes on voids of graphitic materials are produced where the nanoparticles of Au° and Ag° are able to nucleate. Finally, at 800 °C the carbonaceous material disappears, almost for complete and remaining the Au° and Ag° nanoparticles, which as a part of the second step are included in the simultaneous formed on heating, amorphous SiO_2. A schematic representation of the Au° nanoparticles inside the amorphous SiO_2 is shown in Figure 10.

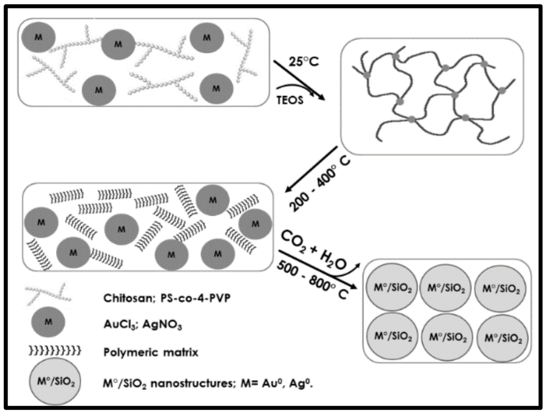

Figure 9. Proposed formation mechanism of the composites Au/SO_2 and Ag//SiO_2.

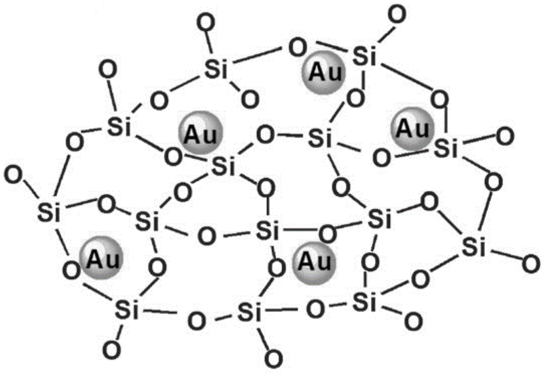

Figure 10. A schematic representation of the Au° nanoparticles inside the amorphous SiO_2.

4.- CONCLUSIONS

The composites Au/SO_2 and Ag/SiO_2 have been conveniently prepared form pyrolysis of the precursors (Chitosan•$(AuCl_3)_n$•$(SiO_2)_m$ and (PS-co-4-PVP)•$(AuCl_3)_n$•$(SiO_2)_m$ and (Chitosan•$(AgNO_3)_n$•$(SiO_2)_m$ and (PS-co-4-PVP)•$(AgNO_3)_n$•$(SiO_2)_m$ in 1:1 and 1:5 molar ratios The nanoparticles of Au and Ag are uniformly distributed inside the Silica matrix and the content of the correspondent Au or Ag can be controlled by the molar metal polymer ratio. A high ratio 1:1 produces a major metal content than the 1:5 ratio metals: polymer. These results are similar to that of bimetallic system Au/Ag//SiO_2[28]. The solid state template Chitosan induce Au ° particle size most smaller (57 nm) than the PS-co-4-PVP template (108 nm) while that for the Ag° nanoparticles no polymer template effect was observed affording nanoparticles as small as 5 nm. A formation mechanism involving the combustion of the organic matter where and reduction of the Au^{3+} and Ag^{+} with the CO (in small amounts produced by incomplete combustion) is proposed.

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