

Bimetallic Au//Ag Alloys Inside SiO₂ Using a Solid-State Method

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Abstract Bimetallic Au/Ag nanostructures have been included inside SiO₂ by pyrolysis of the macromolecular complexes Chitosan·(ML_n/M'L_n)_n·SiO₂ and PSP-4-PVP·(ML_n/M'L_n)_n·SiO₂ with ML_n = AuCl₃ and M'L_n = Ag(CF₃SO₃). The structural characterization was performed by XRD (X-ray diffraction of powder) and UV–Vis, and the microstructural characterization was done by SEM/EDS analysis HRTEM. The resulting products from the pyrolytic precursors PSP-4-PVP·(AuCl₃/AgSO₃CF₃)_n·SiO₂ 1:1 (1), PSP-4-PVP·(AuCl₃/AgSO₃CF₃)_n·SiO₂ 1:5 (2), Chitosan·(AuCl₃/AgSO₃CF₃)_n·SiO₂ 1:1 (3) and Chitosan·(AuCl₃/AgSO₃CF₃)_n·SiO₂ 1:5 (4) were Au/Ag//SiO₂, Au//SiO₂ and Ag//SiO₂ as well as isolated Au and Ag, depending on the polymeric precursor. The Chitosan polymer precursor induces mainly Ag and Ag/SiO₂ nanostructures, while PSP-4-PVP induces mainly Au/Ag//SiO₂ nanostructures. This can be explained by the facility to link Ag⁺ to the NH₂ and OH groups of Chitosan than to the pyridine of PSP-4-PVP. On the contrary, Au³⁺ exhibits most coordination ability to pyridine groups of PSP-4-PVP than NH₂- and OH-groups of Chitosan. EDS mapping analysis indicates a uniform distribution of the Au/Ag nanostructure inside the SiO₂ matrix. Using reflectance diffuse analysis, the plasmon is consistent with the Au/Ag alloys structure.

Keywords State method · Au/Ag nanostructures · Inside SiO₂

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Introduction

Recently, bimetallic nanoparticles (NPs) have received increased attention because of their importance for magnetic, optical, and catalytic applications, as those interesting properties are different from the individual NPs [1]. Several of such applications involve the incorporation of the bimetallic Au/Ag NPs, usually prepared by a solution method, into solid-state devices [2]. This normally involves the evaporation of the solvent leading to agglomeration of the nanoparticles [3–6]. However, solid-state methods to prepare bimetallic Au/Ag NPs are scarce [1, 7], as normally such applications involve the incorporation of the bimetallic Au/Ag NPs into a solid matrix [8]. Over all the known methods of preparation of bimetallic Au/Ag NPs [1], only one was reported to use a solid state route [9]. As a consequence, development of novel solid state methods to produce bimetallic Au/Ag NPs remains a challenge [6].

The main characteristic for an ideal catalyst are: a high surface (for instance a high porous materials) and stable and resistant to high temperatures. In the case of Au/Ag NPs these requirements can be satisfied, for instance, by support these in silica.

Recently, we have developed a novel solid-state method for the preparation of metallic and metal oxides nanoparticles including also bimetallic systems [10, 11]. This method consists in the pyrolysis of macromolecular precursors such as Chitosan·(MLn)_n and PSP-4-PVP·(MLn)_n. Using this method metallic nanostructures of the type M⁰, M_xO_y, depending on the nature of the metal, are obtained. Using Au salts, metallic Au⁰ nanoparticles or metallic foams are obtained while when using Ag complex, Ag⁰ nanoparticles are formed. In addition, when we are able to join two metallic salts as Au and Ag to the polymeric chains of Chitosan and PSP-4-PVP and subsequently the solid macromolecular bimetallic complex is pyrolyzed, bimetallic Au/Ag nanostructures are obtained [7].

In the present manuscript we report a novel solid state method to incorporate bimetallic Au/Ag nanoparticles inside SiO₂ through the pyrolysis of the precursors the macromolecular complexes Chitosan·(MLn/M'Ln)_n and PSP-4-PVP·(MLn/M'Ln)_n with MLn = AuCl₃ and M'Ln = Ag(CF₃SO₃). We have selected the bimetallic Au/Ag NPs due to their most pronounced cooperative properties compared with the another M/M' NP's [1].

Experimental

AuCl₃ and Ag(CF₃SO₃), PSP-co-4-PVP and Chitosan were purchased from Aldrich and used as received. All the reactions were performed using CH₂Cl₂ as solvent.

Precursors Synthesis: Chitosan·(MLn/M'Ln)_n

In a typical synthesis [7], the respective metallic salts AuCl₃ and Ag(CF₃SO₃) were added in a Schlenk tube using CH₂Cl₂ as solvent under magnetic stirring and then

the respective Chitosan amount was added according to the 1:1 (**1**) or 1:5 (**2**) molar ratio. After 7 days, the supernatant solution (if the solid decanted) was extracted with a syringe and the solid was dried under reduced pressure to give a yellow–red solid.

Precursors Synthesis: PSP-4-PVP·(MLn/M'Ln)_n

In a typical synthesis [7] the respective metallic salts AuCl₃ and Ag(CF₃SO₃) were added in a Schlenk tube using CH₂Cl₂ as solvent under magnetic stirring and then the respective Poly(styrene-co-4-vinylpyridine) amount was added according to the 1:1 (**3**) or 1:5 (**4**) molar ratio. After about 6 days the supernatant solution (provided the solid decanted) was extracted with a syringe and the solid dried under reduced pressure to give a solid with diverse colors. In some cases the polymer undergoes an extensive gel formation. In such case the solvent was eliminated at reduced pressure using a high vacuum pump.

SiO₂

SiO₂ was prepared according a literature method [12]. Briefly, tetraethoxysilane (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.

Pyrolysis

The pyrolysis experiments were conducted by pouring a weighed portion (0.05–0.15 g) of the respective mixture precursor Chitosan·(MLn/M'Ln)_n·SiO₂ or PSP-4-PVP·(MLn/M'Ln)_n·SiO₂ 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.

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 microprobe 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. XRD was conducted at room temperature on a Siemens D-5000 diffractometer with θ – 2θ geometry. The XRD data was collected using Cu-K α 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.

Results and Discussion

Figure 1 shows the XRD diffraction patterns of the pyrolytic products from the precursors Chitosan·(MLn/M'Ln)_n·SiO₂ and PSP-4-PVP·(MLn/M'Ln)_n·SiO₂ with molar ratios 1:1. The lattices patterns for both Au and Ag are overlapped and it is not possible to distinguish Au–Ag bimetallic phase from either monometallic phase based on XRD patterns [13–15]. The broad peaks about $2\theta = 20^\circ$ is assigned to amorphous silica [14].

The presence of both Au and Ag was clearly observed by SEM–EDS analysis of the pyrolytic products from Chitosan·(MLn/M'Ln)_n·SiO₂ 1:1 and PSP-4-PVP·(MLn/M'Ln)_n·SiO₂ 1:1 (see Fig. 2). Thus, the morphologies are somewhat dependent on the polymer precursors: with PSP-4-PVP some most disperse grains were observed, while that for the Chitosan precursors, most fused grains were observed.

A detailed inspection was performed by TEM. The composition of the pyrolytic products from all the precursors, identified by EDS, shows the presence of zones with diverse compounds/elements, as shown in Table 1.

From this table for instance for sample 1 nanostructures of Au/Ag//SiO₂ and Au/Ag are observed while that for (3) Ag//SiO₂ and Ag were observed. HRTEM images corresponding to these observations are shown in Fig. 3.

As observed in Fig. 3, different geometries and sizes are observed for the studied pyrolytic products. Au, Ag and Au/Ag nanoparticles are in general spherical, presenting two distribution sizes: the bigger ones ranging from 20 to 100 nm and the smaller ones of typical sizes between 1 and 5 nm. The high phase/morphology found in the products of inclusion of Au and Ag NP's can be due to the high thermal processes, which is known to give nanostructured materials with a wide size and morphologies distribution [6].

The UV–visible absorption spectra in solid state show a single and broad around 410 nm characteristic of Au/Ag bimetallic alloys materials [13, 16, 17]. A

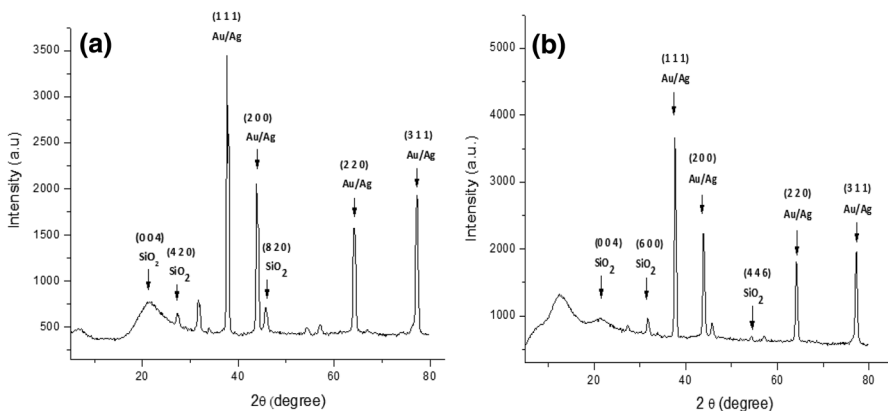


Fig. 1 XRD patterns of pyrolytic products from PSP-4-PVP·(MLn/M'Ln)_n·SiO₂ (a) and Chitosan·(MLn/M'Ln)_n·SiO₂ (b)

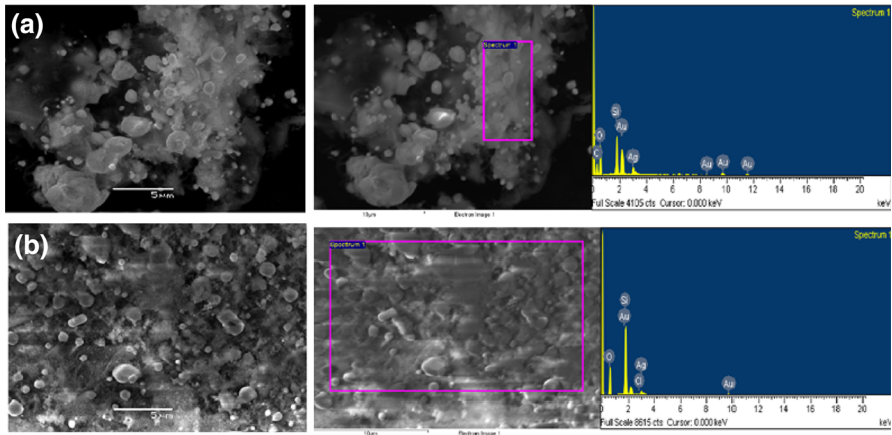


Fig. 2 SEM-EDS image for pyrolytic products from PSP-4-PVP-(MLn/M'Ln)_n·SiO₂ 1:1 (a) and Chitosan(MLn/M'Ln)_n·SiO₂ 1:1 (b)

Table 1 Summary of the pyrolytic products identified by TEM

Sample	Type of structure
(1)	Au/Ag-SiO ₂ ; Ag/SiO ₂ Au/Ag; Au ⁰ ; Ag ⁰
(2)	Au/Ag-SiO ₂ ; Au/Ag; Ag/SiO ₂ ; Ag ⁰
(3)	Au/Ag Ag/SiO ₂ Ag ⁰ ; Au ⁰
(4)	Au/Ag; Au/Ag-SiO ₂

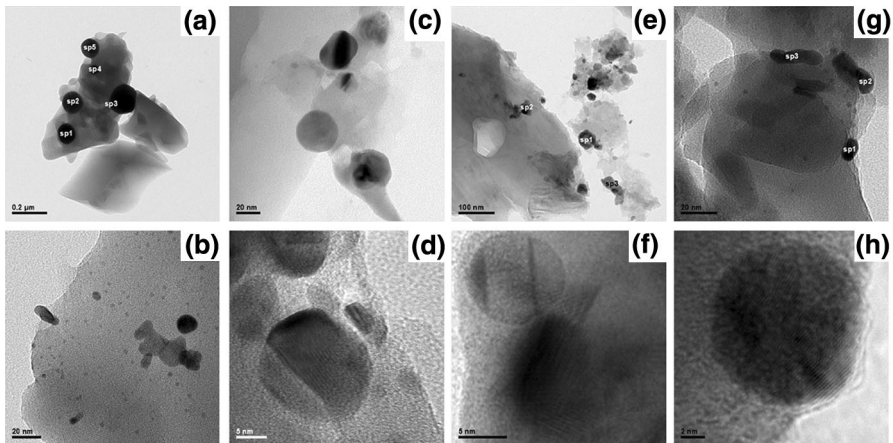


Fig. 3 TEM/HRTEM image of the different pyrolytic products: PSP-4-PVP-(AuCl₃/AgSO₃CF₃)_n·SiO₂ 1:1 (a, b); Chitosan-(AuCl₃/AgSO₃CF₃)_n·SiO₂ 1:1 (c, d); Chitosan-(AuCl₃/AgSO₃CF₃)_n·SiO₂ 1:5 (e, f); and PSP-4-PVP-(AuCl₃/AgSO₃CF₃)_n·SiO₂ 1:5 (g, h)

Fig. 4 Solid-State UV–visible spectra for the pyrolytic product from PSP-4-PVP·(AuCl₃/AgSO₃CF₃)_n·SiO₂ 1:5 (4)

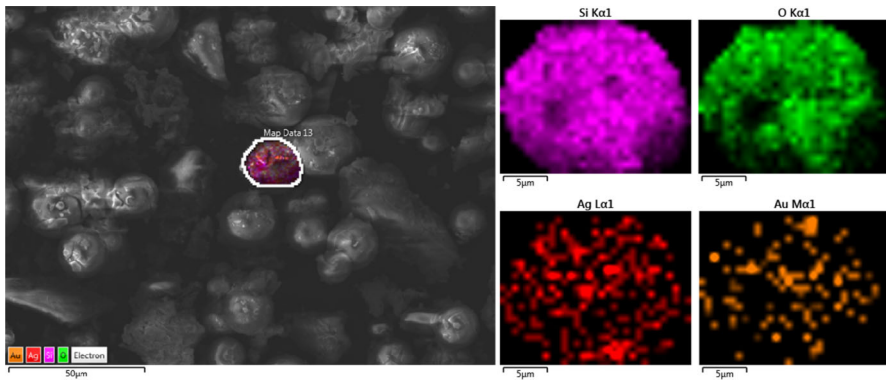
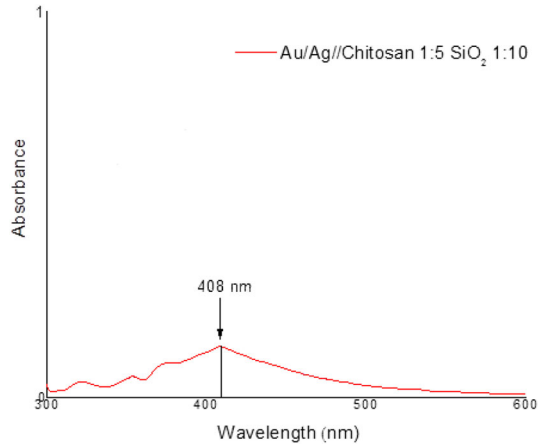


Fig. 5 EDS mapping image for the pyrolytic product from PSP-4-PVP·(AuCl₃/AgSO₃CF₃)_n·SiO₂ 1:5 (4)

representative UV–visible absorption spectrum for the pyrolytic product from Au//Ag//Chitosan//SiO₂ is exhibited in Fig. 4.

Information about the distribution of the bimetallic Au//Ag alloy inside SiO₂ was obtained from EDS mapping analysis. As seen in Fig. 5 for the pyrolytic products from PSP-4-PVP·(AuCl₃/AgSO₃CF₃)_n 1:5 (4) see Fig. 5, the SEM–EDS mapping shows an uniform distribution of the Au/Ag nanostructures inside the SiO₂ matrix. The EDS mapping analysis for the pyrolytic products from the Chitosan complex affords similar conclusions.

Conclusions

Pyrolysis of macromolecular complexes Chitosan(ML_n/M'L_n)_n·SiO₂ and PSP-4-PVP·(ML_n/M'L_n)_n·SiO₂ with ML_n = AuCl₃ and M'L_n = Ag(CF₃SO₃) at 800 °C affords bimetallic Au/Ag included into SiO₂. Depending of the polymer precursors,

different nanoparticles as isolated as Au and Ag could also be obtained. The bimetallic as well as another monometallic NP's are distributed uniformly within the silica matrix. The preparation method of bimetallic Au/Ag included into SiO₂ here described offers an alternative reliable and easy route to include bimetallic M/M' NP's inside SiO₂. Few methods for incorporation of bimetallic Au/Ag NP's inside SiO₂ [14, 18] and another solid matrices [9, 14, 18, 19] all in solution, have been reported.

The method could be a general and easy route to the incorporation of bimetallic M/M' into silica to give suitable materials for different applications in solid-state devices.

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