OXIDATION FACILITY BY A TEMPERATURE DEPENDENCE ON THE METAL NOBLE NANOSTRUCTURED M°/M_xO_y PHASE PRODUCTS USING A SOLID STATE METHOD: THE CASE OF Pd

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ABSTRACT

Pyrolysis at 800°C under air of the macromolecular precursor Chitosan●$(PdCl_2)_n$ and PS-co-4-PVP●$(PdCl_2)_n$ in solid state afford the mixture phases Pt/PdO depending on the molar ratio metal /polymer. For the 1:1 Chitosan●$(PdCl_2)_n$ and PS-co-4-PVP●$(PdCl_2)_n$ precursors the pure phase PdO was obtained while that for another molar ratios 1:5 and 1:10, the mixture phase Pt/PdO were obtained. For the 1:10 PS-co-4-PVP●$(PdCl_2)_n$ precursor the core/shell PdO@Pd nanoparticles as small as 4 nm were observed. Optical properties for the PdO indicate an insulator behavior.

INTRODUCTION

The so called noble metals are resistant to the oxidation and corrosion and include, among other, Pd, Pt and Au. Their ionization potential are in the order Au>Pt>Pd which explain in part their low reactivity. Of these three noble metals Palladium the most reactive and PdO is easily formed by oxidation especially when Pd is finely divided. On the other hand the gold oxides are obtained in extreme conditions by treatment of gold surfaces with oxygen-containing plasma. This reactivity patterns is enhance when the metals are nanostructured. Gold oxide nanoparticles have been obtained treating gold vapors with oxygen in plasma conditions. In our earlier works we have obtained nanostructures M° and metal oxidesM_xO_y starting from the precursors Chitosan●$(MCl_x)_n$ and PS-co-4-PVP●$(MCl_x)_n$ and subsequent solid-state pyrolysis at 800 °C under air. Despite for M= Au and Pt, nanoparticles of Au° and Pt° have been obtained, for M= Pd mainly PdO is obtained, in agreement with the above considerations about this work is described below. Depending on the molar ratio metal / polymer mixture phases Pt/PdO are obtained [1].

Nanostructured Pd, PdO and PdS species have potential applications in catalysis, electronic, and Hydrogen storage [2-5]. More specifically the mixture phase Pd/PdO is usually obtained from solution methods [6-8] and less common from solid state method [8]. Morgado et al. obtained nanostructured Pd/PdO from the metallic complex trans-$[PdCl_2(PEt_3)_2]$ [9], and Schwieger [10] from the complex $[Pd(NH_3)_4Cl_2●4H_2O]$ intercaled into layered aluminum-free silicate Na ilerite. On the other hand solid state preparation of the mixture phase Pd/PdO was achieved from the thermal treatment of the $[Pd(SC_{12}H_{25})_2]_6$ [8]. Liu et al. obtained PdO in pure phase from hydrolysis of $PdCl_2$ in the presence of polyvinylpyrrolidone under microwave irradiation [11].

A number of solution methods have been developed for the synthesis of metal and metal oxides nanoparticles [12-13] but few solid-state have been informed [14]. The application of nanostructured materials to electronic solid-sate devices or to high temperature technology requires, however, adequate solid-state methods for obtaining nanostructured materials [15-20]. Recent studies reported that the evaporation of solvent to obtain Au nanoparticles in solid-state, for an adequate incorporation to a solid-state device -for instance-, results in 3D Au superstructures with properties different to those of Au nanostructures [21-24]. Then, the development of new solid state methods to prepare metallic nanostructured materials is a constant challenge.

The application of nanostructured materials to electronic solid-sate devices or to the high temperature technology requires. However, adequate solid-state methods for obtaining nanostructured materials.In this paper wepresent a novel solid-state preparation method of nanostructured Pd/PdO material, starting from the macromolecular precursor Chitosan●$(PdCl_2)_n$ and PS-co-4-PVP●$(PdCl_2)_n$ and subsequent solid-state pyrolysis at 800 °C under air (see Figure 1) and some optical properties are reported.

EXPERIMENTAL

Synthesis of the macromolecular precursors:

Macromolecular precursors were prepared according previous works [25, 26]. In a typical synthesis the respective metallic salt $PdCl_2$ was added in a Schlenk tube over the CH_2Cl_2 (50 mL) under magnetic stirring and then the respective polymer PSP-co-4-PVP and Chitosan amountwas added, according the 1:1 and 1:5 or 1:10 molar ratio for 15 days at room temperature. After this the supernatant solution was extracted with a syringe and the solid dried under reduced pressure to obtain a dry solid with diverse brown colors. The molar relations indicate the initial stoichiometric relation used in the reagent and not necessarily the coordination degree of the metal in the polymeric chain.

Subsequently, the supernatant solution was extracted with a syringe and the solid was dried under reduced pressure.

Pyrolysis:

The pyrolysis experiments were made by pouring a weighed portion (0.05–0.15 g) of the precursors into aluminum oxide boats that were placed in a furnace (Daihan oven model Wise Therm FHP-12). 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 in each case.

Characterization:

Solid pyrolytic samples were characterized by room temperature X-ray diffraction (XRD) using a Siemens D-5000 diffractometer with θ-2θgeometry and the data was collected using Cu-Kα radiation (40 kV and 30 mA). Images of scanning electron microscopy (SEM) were obtained with a Philips EM 300 microscope; transmission electron microscopy (TEM) analysis was conducted on a JEOLSX100 transmission microscope and infrared spectroscopy (IR) on Perkin Elmer model spectrum BX II. The optical absorbance was measured using a UV-Visible absorption spectrophotometer Shimadzu model Shimadzu UV- 2460 equipped with an accessory for solid samples.

RESULTS AND DISCUSSION

Pyrolysis of the precursors Chitosan●$(PdCl_2)_n$ and PSP-co-4-PVP●$(PdCl_2)_n$ affords Pd or PdO depending on the precursor used and on the metal/polymer ratio, See figure 1.

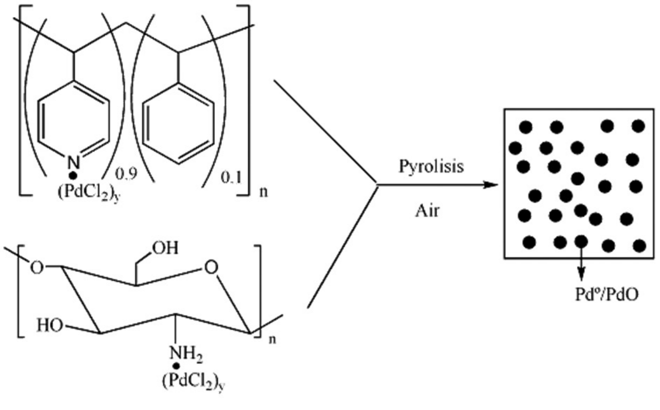

Figure. 1 Diagram of the synthesis in solid state using polymers such as molecular precursors.

The characterization was performed by x-ray of diffraction of all pyrolysis samples and the results are displayed in Table 1.

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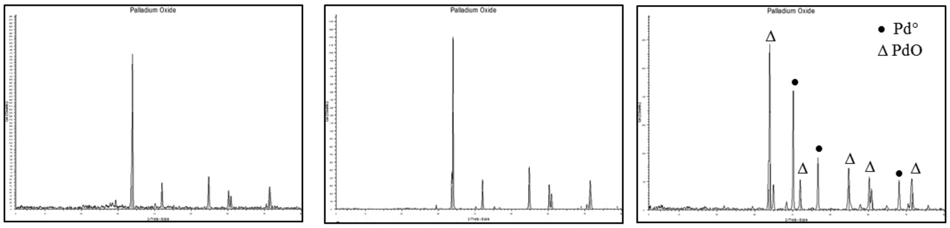
Table 1:

Precursor	N° Compound	Relation M/polymer	Phase mixture
Chitosan•($PdCl_2)_n$	(**1**)	1:1	PdO
	(**2**)	1:5	PdO
	(**3**)	1:10	Pd/PdO
PS-*co*-4-PVP•$(PdCl_2)_n$	(**4**)	1:1	PdO
	(**5**)	1:5	Pd/PdO
	(**6**)	1:10	Pd/PdO

The X-ray of diffraction of pyrolytic products from precursors 1:1 (**1**) and 1:5 (**2**) Chitosan•$(PdCl_2)_n$ and from 1:1 PS-*co*-4-PVP•$(PdCl_2)_n$ (**4**) shows the main typical PdO peaks, at 33.55°, 41.92° and 54.71° assigned to a reflection planes 101, 110 and 112 planes. Can be indexed as indicating the presence of tetragonal PdO with lattice parameters comparable to that of the JCPDS card (00-043-1024) [9,10]. On the other hand, for the precursors (**3**), (**5**) and (**6**) in addition to the peaks corresponding to PdO the peaks at 40.14°, 46.69° and 68.13° can be assigned to a 111, 200 and 220 of palladium syn. JCPDS card (00-046-1043). Four patterns corresponding to the pyrolytic products are shown in figure 2.

This may be due to that relationship 1:5 and 1:10 (metal/polymer) in (**3**), (**5**) and (**6**), there is a greater consumption of oxygen in the combustion. In turn, this produces more CO in the intermediate stage of combustion, which acts as a reducing agent, producing as a result the formation of Pd ° [27-28].


(a) Pd-Qui (1:1) (b) Pd-Qui (1:5) (c) Pd-Qui (1:10)

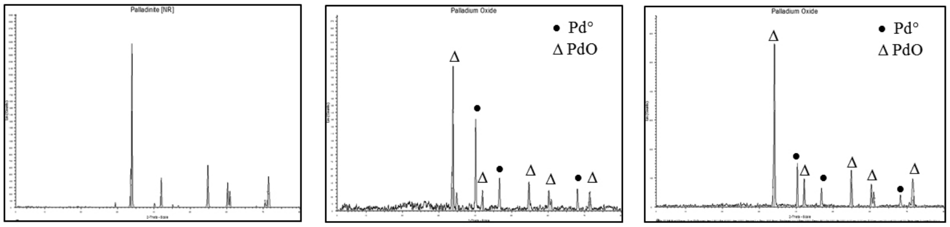
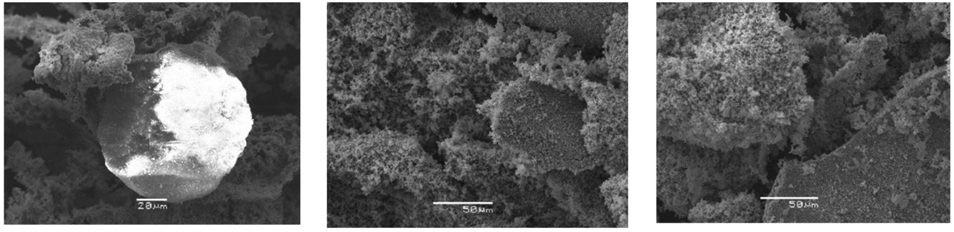

(d) Pd-PVP (1:1) (e) Pd-PVP (1:5) (f) Pd-PVP (1:10)

Figure 2. XRD pattern for the pyrolytic products from Chitosan●$(PdCl_2)_y$ (a) 1:1, (b) 1:5 and (c) 1:10; and PSP-co-4-PVP●$(PdCl_2)_y$ (d) 1:1, (e) 1:5 and (f) 1:10.


(a) Pd-Qui (1:1) (b) Pd-Qui (1:5) (c) Pd-Qui (1:10)

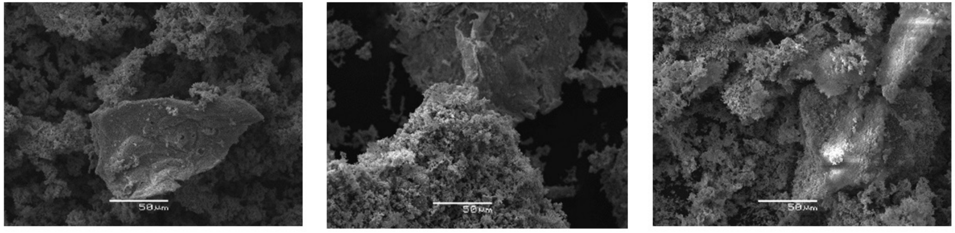
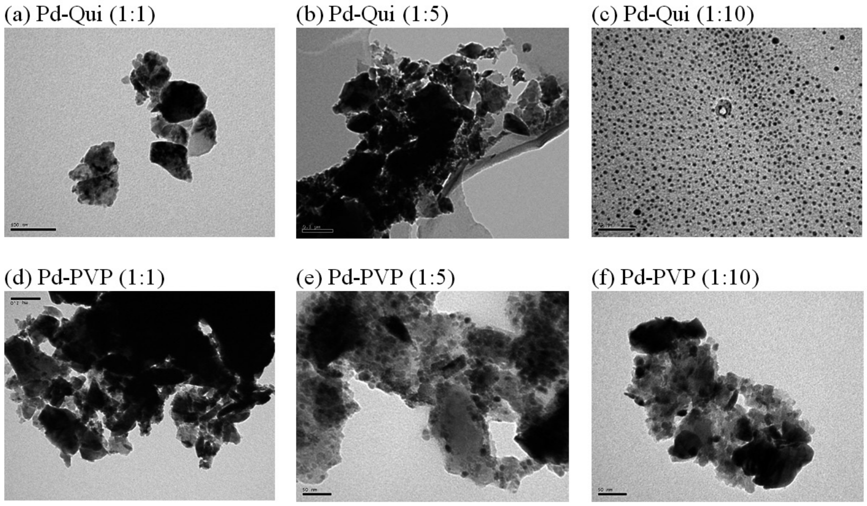

(d) Pd-PVP (1:1) (e) Pd-PVP (1:5) (f) Pd-PVP (1:10)

Figure 3. SEM image for the pyrolytic products from Chitosan●$(PtCl_2)_y$ (a) 1:1, (b) 1:5 and (c) 1:10 and PSP-co-4-PVP● $(PtCl_2)_y$ (d) 1:1 (e) 1:5 and (f) 1:10.

The morphology of pyrolytic products was analyzed by SEM images. In general, a mainly porous morphology for all the (1)–(6) nanostructures PdO and PdO/Pd as is shown in figure 3, was found. On the other hand, the TEM images exhibit irregular shape and varied size nanostructures of Pd/PdO and PdO, with also somewhat agglomerates in some zones (Figure 4 a, b,d-f), as is normally found in solid-state methods. On the contrary, a different situation was observed for the pyrolytic product from the precursor Chitosan●(PdCl$_{2y}$ 1:10 where core shell nanoparticles nanoparticles Pd/PdO as small as 4 nm were observed (Figure 4 c).

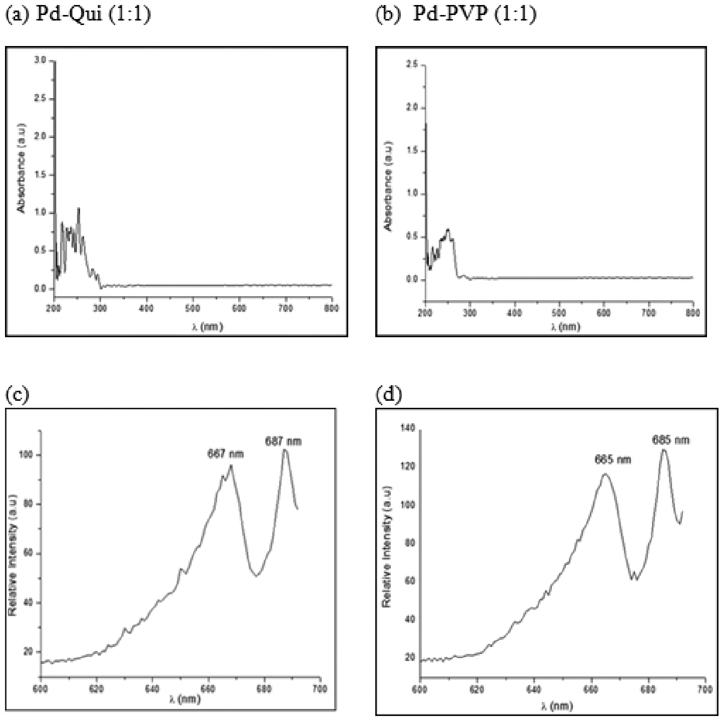
With regard the possible semiconductor behavior of PdO we have measured the Uv-visible spectra and estimated the band gap value using the Tauc approximation [29]. The Uv-visible spectra of PdO from the precursors 1:1 Chitosan•(PdCl$_2$)$_n$ and 1:1 PS-co-4-PVP•(PdCl$_2$)$_n$ are displayed in figure 5 (a) and (b) respectively. Unfortunately the optical data for PdO are scarse, confused and unclear [29, 30], so the comparison with literature data is not possible. Even that, the maxima for PdO 244 nm is consistent with those reported for PdO obtained from Feng Ling and col [31]. Thus the estimated band gap value of 6,15 eV suggests isolating materials for PdO.

Interesting results for the luminescence spectra for PdO [32, 33] obtained from the pyrolityc products from 1:1 Chitosan•(PdCl$_2$)$_n$ and 1:1 PS-co-4-PVP•(PdCl$_2$)$_n$ showing emission maximum at 687 nm and 685 nm with λ excitation of 355 nm are shown in the figure 5 (c) and (d) respectively.


(a) Pd-Qui (1:1) (b) Pd-Qui (1:5) (c) Pd-Qui (1:10)

(d) Pd-PVP (1:1) (e) Pd-PVP (1:5) (f) Pd-PVP (1:10)

Figure 4: TEM image for the pyrolytic products from Chitosan●(PtCl$_2$)y (a) 1:1, (b) 1:5 and (c) 1:10 and PSP-co-4-PVP●(PtCl$_2$)y (d) 1:1 (e) 1:5 and (f) 1:10.


(a) Pd-Qui (1:1) (b) Pd-PVP (1:1)

(c) (d)

Figure 5. Uv-visible spectra of PdO from the precursors (a) Chitosan●(PdCl$_2$)y 1:1 and (b) PS-co-4-PVP•(PdCl$_2$)y1:1 and the emission spectra of PdO from (c) Chitosan●(PdCl$_2$)y 1:1 and (d) PS-co-4-PVP•(PdCl$_2$) y 1:1 using a maximun of the the λ excitation of 355 nm."

CONCLUSION

The morphology of the PdO and Pd/PdO nanostructured materials can be controlled by the metal/polymer ratio of the precursor. For both polymers, SEM shows "porous" in all relations metal:polymer. Chitosan induces the formation of smaller core shell Pd/PdO nanoparticles (4 nm) for the 1:10 molar ratio than for 1:1 and 1:5 ratios. This method is a general alternative for the preparation of Pd nanostructured material in solid state, which could permit ease incorporation to solid matrix for a possible practical application as microelectronic devices and solid high temperature catalyst.

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