SnO_2 thick film gas sensors additivated with noble metal nanoparticles obtained by chemical synthesis

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In this work, Pt nanoparticles obtained by different synthetic routes were incorporated into nanostructured SnO_2 powders by contact transference. The presence of the nanoparticles was confirmed by XRD and TEM. When used as sensitive material in the fabrication of gas sensors, the SnO_2/Pt nanoparticle composites obtained showed a high sensitivity towards the detection of reductive gases such as CO.

Keywords: Thick film gas sensors; Pt nanoparticles; CO detection.

En el presente trabajo, nanopartículas de Pt obtenidas por diferentes rutas de síntesis se incorporaron a polvos de SnO_2 nanoestructurados por transferencia por contacto. La presencia de las nanopartículas fue confirmada por XRD y TEM. Usadas como material sensible en la fabricación de sensores de gases, los compuestos SnO_2/nanopartículas de Pt obtenidos mostraron una alta sensibilidad hacia la detección de gases reductores como el CO.

Descriptores: Sensores de gases; nanopartículas de Pt; detección de CO.

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1. Introduction

Catalytic additives are widely employed to improve the sensing characteristics of oxide-based solid-state gas sensors. The most frequently used additives are noble metals such as Pt, Pd and Au. In thick film techniques, several wet methods have been proposed for introduce the additives into the sensing oxide matrix, most of which are based on two basic procedures:

a) impregnation of the oxide with a salt solution of the additive followed by a heat treatment; and

b) introduction of a salt of the additive during the synthesis of the oxide.

In both cases the additive is introduced as a molecular species ($PtCl_6^-$, $PdCl_2$, etc.) which undergoes a chemical change to its final form, presumably metallic clusters, during a pyrolitic process. However, the final chemical states associated with the additives and their localization in the oxide matrix are issues still under debate [1].

In this work, an alternative approach to the introduction of the catalyst is presented, based on the incorporation of previously synthesized metallic nanoparticles in the formulation of the SnO_2 screen-printing paste. This approach presents, *a priori*, several advantages:

i) the chemically synthesized metal particles are small (typically 1.5-4 nm) and highly catalytic;

ii) the particle size can be controlled by varying the preparative conditions;

iii) different blends of metal clusters can be formulated, opening up the possibility of fine-tuning the sensitivity of the sensors towards different gases; and

iv) the uncertainties concerning the chemical nature, particle size and localization of the catalyst in the fabricated sensor are considerably diminished.

2. Experimental

Three different synthetic routes were employed to produce the metallic nanoparticles:

a) reduction of the chloroplatinic acid in ethylenglycol at 150°C in N_2 atmosphere [2];

b) methanol reduction of a water-methanol solution of a salt of the metal, with poly(N-vinyl-2-pyrrolidone) (PVP) as stabilizer [3];

c) two-phase synthesis based on the transfer of a chloride complex of the metal from the aqueous phase to toluene using tetraoctylammonium bromide as phase transfer reagent; followed by reduction with $NaBH_4$ [4].

Suspensions of SnO_2 (Aldrich P.A.) and the Pt nanoparticles (0.5 – 1%) were thoroughly mixed by magnetic stirring. The composites were decanted, filtered and calcined at 550°C. The powders were characterized by X-ray diffraction (XRD) and transmission electronic microscopy (TEM).

Thick film pastes were obtained by mixing the composites with a suitable organic vehicle [5]. The sensitive pastes

thus obtained were screen-printed onto 96% alumina substrates, covering interdigital electrodes of Pt. The gas sensing properties of the sensors were measured in a flowing gas system at a flow rate of 500 ml/min at various concentrations of different reducing gases. All the electrical resistance measurements were performed in the temperature range 250-350°C in a sealed Teflon chamber.

3. Results

All three synthesis methods yield very stable colloids of Pt nanoparticles. In the obtention of the screen-printing pastes, however, the nanoparticles obtained by method (a) presented advantages due to a higher metal concentration, better compatibility with the organic vehicle, and a more effective contact transference to the SnO_2.

In Fig. 1, typical XRD spectra of a composite SnO_2/ Pt nanoparticles is shown. The XRD diffraction pattern revealed that tin dioxide cassiterite present an average crystal grain size of 60 nm. The XRD pattern also shows two diffraction signals due to the Pt nanoparticles. The intensity of the signals is very low and strongly depends on the size and concentration of the Pt nanoparticles.

The micrographs obtained by transmission electron microscopy (TEM) show that the sizes of the SnO_2 nanocrystals vary widely in the range 20-100 nm, with an average value of 60-70 nm. This value corresponds quite well with that obtained from the XRD diffraction patterns. In Fig. 2, a high magnification TEM image of one of the samples is shown. The micrograph shows an agglomeration of tin oxide nanocrystals with an average size of 40 nm. The grains are covered by Pt nanoparticles with an apparent diameter of 4 nm. It is interesting to note that the nanoparticles are somehow aligned onto the surface forming "nanoleads". This

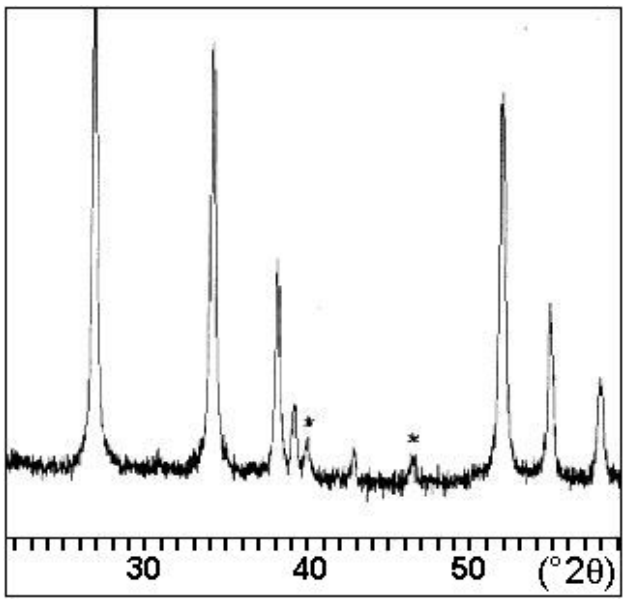

FIGURE 1. XRD of SnO_2 modified with Pt nanoparticles (1% w/w). The peaks assigned to Pt are indicated with (*).

TABLE I. Sensitivity R_{air}/R_{CO} of SnO_2 gas sensor modified with Pt nanoparticles(1% w/w) to different concentrations of CO.

R_{air} (Kohm)	Sensitivity			
	50 ppm	100ppm	300 ppm	475 ppm
79.54	3.8	5.4	9.9	13.4

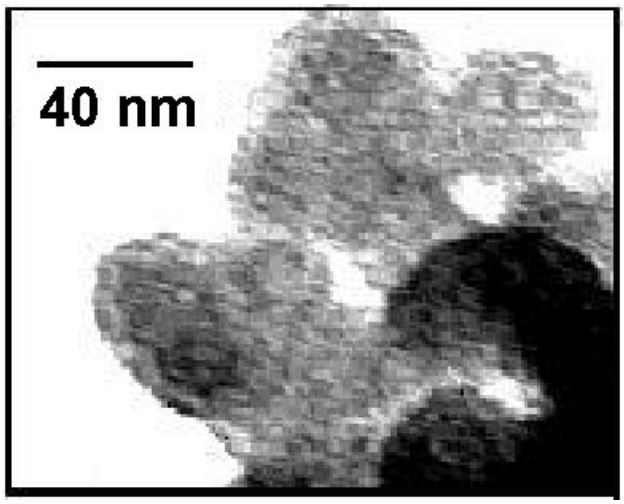

FIGURE 2. TEM image of Pt nanoparticles adsorbed onto SnO_2.

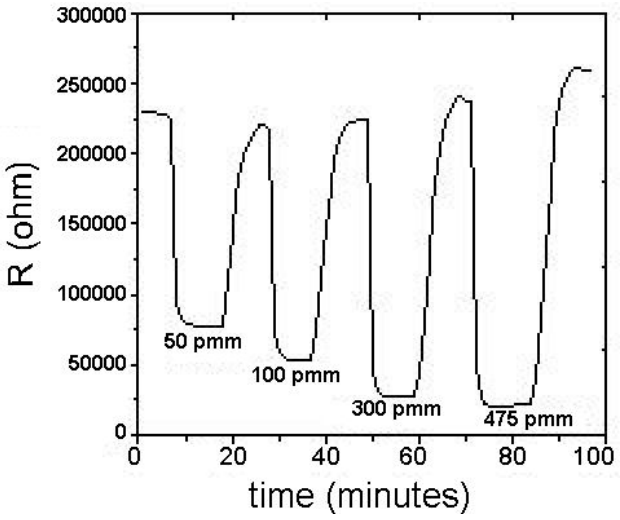

FIGURE 3. Response of SnO_2 gas sensor modified with Pt nanoparticles (1% w/w) to different concentrations of CO.

is probably a decoration effect due to the preferential deposition of the Pt nanoparticles along imperfections in the SnO_2 nanocrystals, where the electrostatic oxide-Pt nanoparticles interactions are stronger.

Figure 3 shows a typical response of SnO_2/Pt nanoparticles (1% w/w) when the sensor is exposed to different CO concentrations, and indicates that the sensor presents a good response to CO. Table I summarizes the values of the resistance in air (R_{air}) and the relative sensitivity defined as R_{air}/R_{gas} at different CO concentrations. Further research is

in progress in order to optimize the nanoparticle transference and to improve the sensor selectivity using blends of metallic nanoparticles.

4. Conclusions

In the present work stable colloids of Pt nanoparticles have been obtained by three different chemical routes. The Pt nanoparticles were transferred to the surface of SnO_2 by electrostatic contact. The composites SnO_2/Pt nanoparticles are highly sensitive towards a redactor gas as CO. The sensors fabricated present a good sensitivity a high potential of improvement.

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