

Synthesis and characterization of catalytic shells self assembled onto nano-sized SnO₂ cores

C.A. Moina¹, L.B. Fraigi², A. Weinstock²

¹Instituto Nacional de Tecnología Industrial, INTI- Electrodeposición y Procesos Superficiales, Argentina.

²Instituto Nacional de Tecnología Industrial, INTI- Electrónica e Informática, Argentina.

*C. Moina, Phone : +5411 4754 , email: moina@inti.gov.ar

Abstract

SnO₂ nanopowders were surface modified with derivatives of the propionic acid. 3-mercaptopropionic, 2-mercaptopropionic, 3-aminopropionic and 2-amino-3-mercaptopropionic acids were used as modifiers. Pt nanoparticles were self-assembled on the functionalized SnO₂. The self-assembling of the metallic nanoparticles was confirmed by FTIR and TEM. The attachment of the Pt clusters to the functionalized oxide was strongly dependent of the molecular linker. The differences in reactivity can be explained in terms of the structural characteristics of the surface complex formed.

Keywords: Metal nanoparticles additivated SnO₂, functionalized SnO₂, gas sensors

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 to introduce the additives in the sensing oxide matrix have been proposed, most of which are based in two basic procedures: a) impregnation of the oxide with a salt solution of the additive followed by a heat treatment [1]; and b) introduction of a salt of the additive during the synthesis of the oxide [2,3]. In both cases the additive is introduced as a molecular species (PtCl₆⁻, PdCl₂, etc.), which undergoes a chemical change to its final form, presumably metallic clusters, during a pyrolytic process.

Recently we have proposed a new method to attach catalytic nanoparticles to the surface of SnO₂ nanocrystals [4]. Briefly, in a two steps procedure a catalytic shell is formed on the surface of an oxide core. The shell consists of a self-assembled monolayer of a molecular linker, which provides anchorage to the catalytic metallic clusters. The core-shell assembly can be used as the starting

material for manufacturing sensors with improved characteristics.

This approach presents several advantages: i) the chemically synthesized metal particles are small (typically 1.5-4 nm) and highly catalytic; ii) the catalyst load can be easily controlled by varying the self-assembling conditions; and iii) different blends of metal clusters can be formulated, opening the possibility of fine-tuning the sensibility of the sensors towards different gases. In the present communication both, the synthesis procedures to obtain the dual systems and its characterization by infrared spectroscopy are described in detail.

Experimental

SnO₂ (Merck $\phi \cong 50$ nm), colloidal Pt nanoparticles (glycol method, $\phi \cong 4$ nm) and mercapto and amino derivatives of the propionic acid (3-mercaptopropionic, 2-mercaptopropionic, 3-aminopropionic and 2-amino-3-mercaptopropionic acids, p.a. grade) were used in the different experiments.

Synthesis of Pt nanoparticles

Pt metallic nanoparticles (NP Pt) were obtained by reduction of the chloroplatinic acid in ethylenglycol at 150° C in N₂ atmosphere. The experimental details were published elsewhere[4].

Functionalization of SnO₂

a) *Cysteine*: SnO₂(Merck) was placed in contact with a methanolic solution of cysteine (cys, 2-amino-3-mercaptopropionic acid.). The molar ratio was fixed at 1:3. The pH was adjusted at 8 with a methanolic solution of NaOH 0.5M. The mix was stirred for 3 h. The resulting precipitate was decanted, washed several times with methanol and dried at 70°.

b) *Alanine*: SnO₂ and an aqueous solution of alanine (3-aminopropionic acid) in a molar ratio 1:3 were stirred for 3 h. The pH was kept at 4.5. The precipitate was decanted, washed with water and dried at 70°.

c) *3-MPA*: SnO₂ and an aqueous solution of 3-mercaptopropionic acid, molar ratio 1:2, were stirred for 3 h. The pH was kept at 5. The precipitate was decanted, washed with water and dried at 70°.

d) *2-MPA*: SnO₂ and an aqueous solution of 2-mercaptopropionic acid, molar ratio 1:2, were stirred for 3 h. The pH was kept at 5. The precipitate was decanted, washed with water and dried at 50°.

Self assembling of Pt NP

The chemically modified SnO₂ powders were suspended in methanol and sonicated by 10'. A solution of Pt NP was added in order to obtain a ratio SnO₂: Pt 100:1 p/p. The mixes were stirred for 3 h, decanted by centrifugation, washed three times with methanol and dried at 50°. The final colour of the powders varied from dark to pale grey, depending on the molecular linker.

The powders thus obtained were characterized by transmission electron microscopy (TEM) and diffuse reflectance-absorption infrared Fourier transform spectroscopy (DRIFT).

Results

TEM

The presence of metallic particles on the surface of the SnO₂ has been confirmed by TEM. In Figure 1 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 50 nm. The grains are covered by Pt nanoparticles with an apparent diameter of 4 nm.

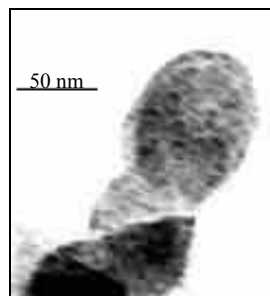


Figure1-TEM image of Pt nanoparticles onto of SnO₂

It is interesting to note that the NP are somehow aligned onto the surface forming “nanoleads”. This is probably a decoration effect due to the preferential deposition of the NP along imperfections in the SnO₂ nanocrystals, where the electrostatic interactions oxide-Pt NP are stronger.

FTIR

Is in general accepted that the carboxylic acids anchor oxides through the carboxylate moiety [5,6]. The infrared spectra of the adsorbed carboxylate ion has a strong antisymmetric (vas) and medium intensity symmetric (va) stretch absorption at 1650-1510 and 1450-1250 cm⁻¹, respectively. There are three common coordination modes: unidentate, chelating bidentate and bridging bidentate. The presence of functional groups with complexing properties (such as -NH₂ and -SH, in the present case) can led to the formation of complex surface structures involving more than one group [7].

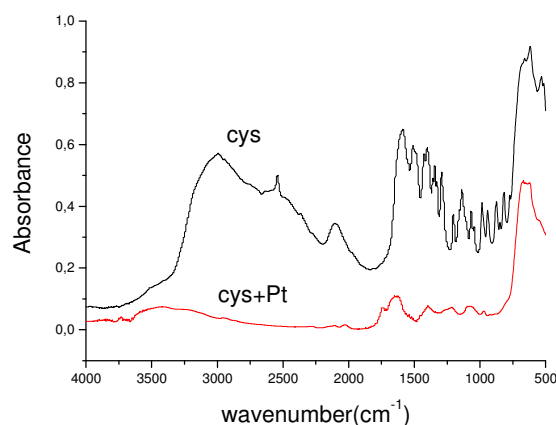


Fig.2:FTIR spectra of SnO₂/Cys and SnO₂/Cys/Pt

In Figure 2 the infrared spectra of SnO₂ functionalized with cysteine is shown. Several distinctive bands can be observed. The broad band centered at 3000 cm⁻¹ can be assigned to the stretching modes of the -N-H bonds, while the band at around 2550 cm⁻¹ corresponds to the stretching of the S-H bond [8]. The band at 2100 cm⁻¹ indicates the presence of extensive hydrogen bonding due to the amino groups. The fingerprint region shows a complex vibrational structure. The bands at 2585 and 1420 cm⁻¹ can be assigned to the asymmetric and symmetric stretching modes of the adsorbed carboxylate moiety; while the bands around 1500 cm⁻¹ are deformation modes of the amino group [8]. From the spectra can be concluded that the cysteine is anchored through the carboxylate, with the amino and thiol groups relatively free for further reaction. When Pt NP are self-assembled onto the modified SnO₂ the DRIFT spectra depicts changes in the bands. Noteworthy, the band at 2550 cm⁻¹ is absent indicating that the cysteine molecules are coordinated to the Pt NP through the sulfur of the thiol moiety. On the other hand, there is a noticeable quenching of the bands due to the amine (at 3000, 2100 and 1500 cm⁻¹). This suggest that the amino group is also involved in the bonding to the Pt NP. Interestingly, a new band appears at around 1740 cm⁻¹ that is indicative of the stretching of the C=O. Thus in the new configuration cysteine forms an unidentate complex with the SnO₂ while the Pt NP are bonded through the -N and the -S forming a five-membered ring. Has been noted that planar five-rings are stable structures [7].

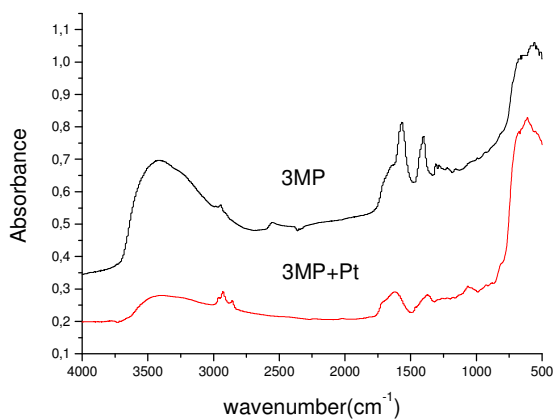


Fig.3: FTIR spectra of SnO₂/3MP and SnO₂/3MP/Pt

In Figure 3 the infrared spectra of 3-MPA/SnO₂ and 3-MPA/SnO₂/Pt NP are shown. In the first case, there is a band centered at 3400 cm⁻¹ which indicates that the surface is heavily hydroxylated. There is a band at 2550 cm⁻¹ due to the -S-H bond

and a group of bands and shoulders in the region 1750-1350 cm⁻¹ probably due to the coexistence of more than configuration of the carboxylate. When the Pt NP are assembled, the band at 2550 vanishes indicating the formation of -S-Pt bond. The two broad bands centered at 1620 and 1370 cm⁻¹ correspond to the vas and va of the carboxylate, respectively.

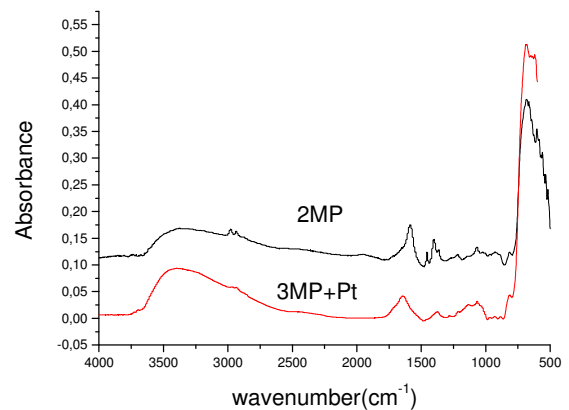


Fig. 4: FTIR spectra of SnO₂/2MP and SnO₂/2MP/Pt

In Figure 4 the spectra of the 2-MPA systems are shown. The most prominent feature is the disappearance of the band due to the S-H stretching at 2550 cm⁻¹, even in the absence of Pt NP. Then, it is apparent that the -SH in α position contributes to the anchoring of the acid to the oxide. This can explain the low affinity toward Pt binding of the SnO₂ functionalized with 2-MPA.

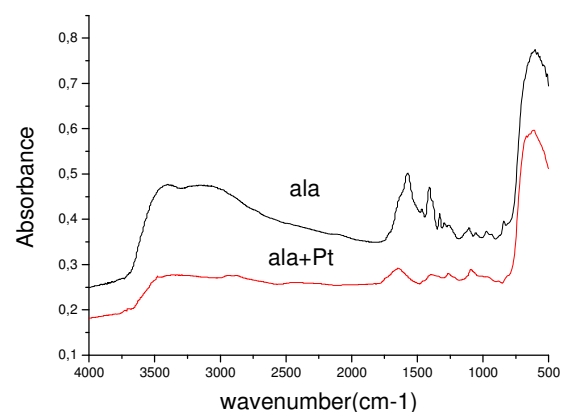


Fig.5: FTIR spectra of SnO₂/Ala and SnO₂/Ala/Pt

Figure 5 shows the infrared spectra of SnO₂/alanine and SnO₂/alanine/Pt NP. In the first case, the spectra

depict a broad band centered at 3100 cm^{-1} and a band at 1570 cm^{-1} that can be assigned respectively to the stretching and deformation modes of the amine [9]. The shoulder at around 1640 cm^{-1} and the band at 1400 cm^{-1} corresponds to the stretching modes of the carboxylate. When Pt NP are assembled, there is a noticeable quenching of the bands due to the amine modes, suggesting that Pt is bonded through the $-\text{NH}_2$.

Discussion

The derivatives of the propionic acid studied presents different affinities toward the Pt NP. In order of decreasing affinity: Cys > 3-MPA > Alanine > 2-MPA.

Cysteine shows a strong binding to Pt, perhaps due to a five membered ring where both, $-\text{NH}_2$ in position α and the $-\text{SH}$ in position β are involved. This bi-functional complex seems to be highly stable, leading to a quantitative transfer of the NP toward the modified oxide. 3-MPA is also an effective monodentate ligand that form stable bonds with the thiol group. Alanine on the other hand is not as effective as ligand. This is due to the limited affinity of the amines toward Pt, as compared to thiols. The 2-MPA presented the poorest affinity for Pt NP, despite the presence of a thiol group. The lack of reactivity seems to be related to the tendency of the $-\text{SH}$ to bind to the oxide. To effectively attach to the Pt NP, the surface complex must rearrange which is probably energetically too costly to be effective.

Conclusions

The effectiveness of different bi- and three-dentate ligands to bind SnO_2 and Pt NP is

dependent on the structural characteristics of the complexes formed on the surface of the oxide. The thiol group in β position presents a higher affinity toward Pt NP. This effect is reinforced by the presence of ligands like $-\text{NH}_2$ in α position.

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