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TiO₂ sol-gel thin films containing Au and Pt nanoparticles with controlled morphology: optical study and gas sensing properties

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ABSTRACT

Au and Pt nanoparticles are prepared with colloidal techniques in order to achieve high morphological quality, capped with a polymer and then embedded inside a TiO₂ sol-gel matrix, resulting in a homogeneous dispersion of both metal colloids, confirmed by TEM analyses. Refractive index values measured with ellipsometry increase with the annealing temperature, with quite a linear trend, and at the same time the Au surface plasmon resonance peak undergoes a red shift: the refractive index evaluated from the Au plasmon band is slightly lower than the measured value, indicating that the refractive index just around metal particles is different from the average of the matrix, likely because of the polymeric capping agent. Optical gas sensing tests towards CO and H₂ are presented as one of the possible applications of these nanocomposites.

Keywords: Gold, Platinum, TiO₂, nanocomposite, sol-gel, optical sensor.

1. INTRODUCTION

Interaction between noble metal nanoparticles (NPs) and transition metal oxides is a topic widely studied in materials science research, due to multiple applications in such fields as catalysis [1], sensing [2], optical amplification [3]. Oxides like WO₃, ZnO, TiO₂, doped with noble metal nanoparticles have been prepared with many different techniques, for example sputtering [4], spray pyrolysis, [5], CVD [6], sol-gel [7].

However, these techniques usually suffer of poor control on the materials' morphology in terms of dimension, shape, size dispersity and aggregation phenomena. In this paper we report a synthesis of sol-gel TiO₂ thin films doped with Au and/or Pt nanoparticles prepared using colloidal methods and eventually introduced inside the solution, in order to control and tailor metal NPs properties, improving the overall quality of the nanocomposite.

Pt is probably the best known and widely adopted catalyst in oxo/reductive processes of a variety of gases such as CO (catalyzers for automotive exhausts) or H₂. It is known that in colloidal form Pt is an excellent catalyst for hydrogen reactions. The colloidal form, with its very large surface area per unit weight, is essential to the catalytic action. Historically Pt was used in a wide variety of applications, from the manufacture of catalytic sulphuric acid (oxidizing SO₂ to SO₃) to the nitric acid manufacture (oxidizing NO to NO₂), as well as in petroleum refining (catalytic cracking).

Au is not specifically a catalytic material, although the debate about catalytic properties of small Au particles is still in progress; but gold is probably the most studied metal in materials science, because of its strong Surface Plasmon Resonance (SPR), especially when it is localized on the surface area of small clusters (localized-SPR). This fact, in addition to the high chemical stability of Au NPs, has raised the use of gold in many different applications like sensing [8,9], photocatalysis [10,11], SERS[12,13].

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There is a wide literature about Au and Pt NPs synthesis, in aqueous, alcoholic and organic media, using different strategies to control the particles nucleation and growth and to prevent their aggregation, such as encapsulation in dendrimers [14-15] or capping with polymers, thiols or amines [16-20].

The aim of this paper is to provide a simple route to prepare thin films doped with Au and Pt nanoparticles with good control on morphological aspects of both matrix and dopant materials; such a process can be extended to several dielectric-metals nanocomposites, acting on the capping molecules of the NPs and on the chemistry of the sol-gel precursors used for the matrix synthesis. Preliminary gas sensing tests are here presented.

2. EXPERIMENTAL

Gold colloids of about 10 nm diameter were prepared according to the Turkevich method [21] by reducing HAuCl_4 with trisodium citrate in water; 10.000 g/mol average molecular weight poly(N-vinylpyrrolidone) (PVP) was used as stabilizing agent according to the ratio $\text{gPVP/molAu} = 1000$. The solution was centrifuged at 14000 rpm to precipitate Au NPs; the supernatant was then discarded and the particles were eventually re-dispersed in ethanol. This procedure was repeated up to three times in order to remove all the excess water. After the washing procedure the NPs were suspended in EtOH to obtain a 22.7 mM particles concentration.

Platinum colloids were synthesized dissolving $(\text{H}_2\text{PtCl}_6)$ in methanol (0.45 mM) in presence of PVP according to the ratio $\text{gPVP:molPt} = 500$, followed by slow reduction of PtCl_6^{2-} ions by means of SuperHydride solution (1.0 M solution of lithium triethyl borohydride - LiBEt_3H - in THF). Synthesis was then followed by concentration of the NPs suspensions up to 7 mM by slow evaporation of the solvent in a rotary evaporator.

A two-step, acid-based recipe for TiO_2 has been adopted, based on the chemistry of Ti-isopropoxide. In detail, a first mixture of Ti-isopropoxide and Acetic Acid (HOAc) was made, according to $\text{Ti} : \text{HOAc} = 1 : 5.7$ (molar), and stirred for 45 minutes. Subsequently a due amount of IsoPropyl Alcohol (IPA) according to $\text{Ti} : \text{IPA} = 1 : 1.35$ (molar) was added and the final solution stirred for a further 20 minutes. At this point the Au-PVP and/or Pt-PVP NPs suspensions were added to the sol-gel solution according to $\text{Ti} : \text{Au} : \text{Pt} = 1 : 0.085 : 0.026$ molar ratio. In a typical preparation, 0.13 mL of the Ti mother batch were mixed with 0.65 mL of the Au suspension and 0.65 mL of the Pt suspension.

The mixture was used to deposit films via spin-coating on SiO_2 substrates under a constant nitrogen flux, at 3000 rpm for 25 seconds. The films underwent subsequent thermal treatment in air at temperatures in the 100°C - 500°C range annealed directly at the target temperature. A series of films containing both Au and Pt NPs together with films containing either Au or Pt NPs and films of pure TiO_2 have been obtained. To prepare films of pure TiO_2 , MeOH was used to replace the NPs aliquots so that the overall mixture volume ratio was retained. In a similar fashion, MeOH replaced either the Au or the Pt suspension aliquots to get films containing only one kind of metal.

The samples realized for the optical gas sensing measurements were obtained spinning 3 layers of the above mixture, stabilizing each layer on a hot plate (200°C) for 10 seconds.

Colloidal NPs and final films have been characterized by TEM using a Philips CM10 transmission electron microscope. The collection of an image of the film doped with Au and Pt NPs was made possible by spin-coating a carbon-coated copper grid with the sol-gel solution. Extinction spectra were collected using a Cary 5 UV-vis-NIR spectrometer in the 200–900 nm wavelength range. Ellipsometric measurements were carried out using a Jobin-Yvon UVISSEL spectroscopic ellipsometer and the data were fitted to standard dispersion formulae. Optical gas sensing tests to 0.1% v/v (1000 ppm) CO and H_2 balanced in dry air at 300°C operative temperature were performed by making optical transmittance measurements on samples mounted inside a custom-built gas flow cell coupled with a Varian Cary1E spectrophotometer. Details are reported elsewhere [22].

3. RESULTS AND DISCUSSION

The citrate reduction of gold precursor in water provides a simple method to obtain quite monodisperse nanoparticles in a wide range of sizes by solely varying the ratio between HAuCl_4 and sodium citrate [23]. The colloids synthesized for this study have a mean diameter of 13 nm, with a standard deviation of 8%, as can be envisaged in Figure 1a. As far as Platinum is concerned, although the synthesis with thiols seems to be the most widely adopted to produce Pt NPs of a good morphological quality and stability, in the present study an alternative synthetic route is presented, which adopts PVP as stabilizing agent instead of thiols. This decision was made because PVP is highly soluble in sol-gel suitable

solvents, i.e. alcohols, granting immediate dispersion of Pt in these solvents, and because sulfur may poison Pt, as it is known for Pt-based industrial catalysts, thus reducing its reactivity toward gases.

Because Pt NPs SPR frequencies are in the deep UV region [24], a direct monitor of the SPR band was not possible in this case and it had to be done indirectly by observing the consumption of Pt ions in solution, which on the contrary exhibit strong optical signal arising from solvated PtCl_6^{2-} ions [16]. The reduction of Pt^{4+} by LiBEt_3H was confirmed by the complete disappearance of such band [25]. A brief study was carried out to isolate the proper amount of PVP needed to avoid particle aggregation and to narrow the size distribution, giving the ratio $\text{gPVP}:\text{molPt} = 500$ as the best result. A TEM image of the Pt NPs used for this study is reported in Figure 1b.

Figure 1. Bright field TEM images of a) Au NPs (the scale bar is 50 nm); b) Pt NPs (the scale bar is 20 nm).

Regarding TiO_2 synthesis, acetic acid was used as the complexing agent because acetate groups can replace isopropoxy groups, thus creating a soluble species with much lower reactivity than the starting Ti-isopropoxide [26] according to:

showing that the liberated isopropoxy groups enter solution as iso-propanol. This reaction is rapid and quite exothermic in nature. Eventually, some type of trans-esterification reaction is likely to occur. In this case, titanium bonded isopropyl and acetate ligands can participate in a condensation reaction, also yielding isopropyl acetate as a byproduct:

Through this path a direct condensation of TiO_2 is thus observed, but related reactions can occur between free acetic acid and bound isopropyl groups or free alcohol and bound acetate:

These related reactions yield highly reactive Ti-OH groups that will rapidly condense to form Ti-O-Ti bridges.

The two step synthesis was adopted to promote complete condensation of Ti-O-Ti groups: the first step induces substitution of propoxy groups with acetate terminations according to reaction (1), which is naturally followed by condensation of Ti-O-Ti through reaction (2), and the second step consists in a post addition of IPA to further promote Ti-O-Ti formation due to reactive Ti-OH groups produced in reaction (4).

Noble metals nanoparticles are added just before deposition, so the chemistry of the sol-gel solution is not largely affected. TEM characterization has been useful to directly evaluate the NPs homogeneous distribution inside the hosting TiO_2 film. A TiO_2 -Au-Pt film has been directly deposited on the back of a carbon coated TEM grid and annealed up to 200°C ; then the grid was imaged by TEM and the results are presented in figure 2. Both Au and Pt NPs are clearly visible in the image, the NPs distribution inside the matrix appears to be homogeneous and both particles dimensions and shape are retained from the starting NPs solution. It is therefore clear that TEM confirms that NPs of the two metal

species have been successfully embedded inside a common matrix, with absence of NPs aggregation or segregation of Au rich areas from mostly Pt populated ones. All the NPs of both species appear to be equally, homogeneously and statistically distributed inside the host matrix.

Figure 2. Bright field TEM image of TiO₂-Au-Pt film annealed at 200°C. The scale bar is 20 nm.

The evolution of the optical properties of the nanocomposite film has been monitored through UV-visible absorption measurements. Figure 3 reports absorption spectra measured for undoped TiO₂, TiO₂-Pt and TiO₂-Au films.

Absorbance spectra of undoped and Pt-doped films are mainly featureless in the visible region, while absorbance spectra of TiO₂ films containing Au NPs present a clear optical feature due to the SPR band of embedded Au. The spectra depict the progressive evolution of the SPR band according to an increase of the annealing temperature. A steady red-shift of its maximum together with an increase in its intensity are clearly evidenced. The dotted vertical line refers to the position of the SPR maximum recorded for Au NPs as synthesized in aqueous media (522 nm). The progressive evolution of the TiO₂ structure at increasing annealing temperatures leads to an increase of its refractive index, which in turns provokes a shift in the plasmonic frequencies of the surface conduction electrons of embedded Au NPs.

Figure 3. Absorbance spectra of a) TiO₂; b) TiO₂-Pt and c) TiO₂-Au samples annealed the different temperatures (a=100°C, b=200°C, c= 300°C, d=400°C, e=500°C).

All spectra show a definite band-gap in the UV range in the 360-370 nm region, corresponding to a bandgap value of 3.3-3.4 eV (in agreement with values reported elsewhere [27] for nanocrystalline TiO₂ films). It is possible to recognize a weak increase of such band-gap with increasing annealing temperature, to be related to the thermal evolution of the TiO₂ structure.

Figure 4. Absorbance spectra of TiO₂-Au-Pt samples series (straight lines). Undoped TiO₂ spectra as dotted lines are also reported

Figure 4 refers to absorbance spectra of TiO₂ films containing both Au and Pt NPs. As in the previous case, the optical absorbance spectra of TiO₂ containing both metallic NPs are dominated by the strong absorption band Au NPs and again the SPR band red-shifts according to an increase in annealing temperature. If the SPR band maximum position measured for all the films is plotted versus the annealing temperature, it is possible to directly evaluate the combined effect of annealing process and of film composition on the overall optical properties of films. Figure 5a shows that the evolution of the SPR band maximum is perfectly linear with the increasing annealing temperatures of films in all cases. There is indeed a clear blue-shift of SPR band maximum position registered in films containing both Au and Pt NPs if compared to films containing only Au NPs. A constant gap is observed if band positions of Pt and non Pt containing films are compared at the same annealing temperature. It could be possible to conclude that the presence of Pt decreases the refractive index of the Au NPs hosting media increasing the overall film porosity due to introduction of extra PVP compared to films containing only Au NPs. In fact, knowing that the refractive index of Pt in the 480-680 nm spectral region is in the 1.91-2.5 range [28], it seems unreasonable to propose that Pt lowers the overall refractive index.

The refractive index of the Au NPs surrounding matrix has been estimated from the SPR band position by means of the Mie theory [29] and compared to the refractive indexes measured through ellipsometry. A comparative plot of the obtained values as a function of the annealing temperature of the films is presented in Figure 5b.

Calculated refractive indexes from SPR data are slightly lower if compared to those measured with the ellipsometer. This can be related to the fact that values calculated using SPR parameters refer to the dielectric nature of the immediate surrounding of the Au NPs, while those measured with ellipsometry are related to an average value mediated on the whole TiO₂-NPs system. Furthermore, both measured and calculated refractive indexes of TiO₂-Au are substantially higher than those of TiO₂-Au-Pt films, in all cases. This indicates that not only the immediate surroundings of Au NPs are characterized by lower refractive index when Pt NPs are present, as previously commented, but that the whole matrix with embedded NPs presents a lower refractive index when Pt NPs are present, as ellipsometry measurements refer to

values mediated on the whole material. This in turn enforces the hypothesis that extra PVP introduced with Pt NPs leads to formation of a more developed film porosity.

Figure 5 a) SPR wavelength position versus annealing temperature for TiO₂-Au and TiO₂-Au-Pt. b) Values of refractive indexes measured with the ellipsometer compared to those evaluated using the SPR band position from absorbance spectra for the two series of samples.

TiO₂ layers containing Au-PVP and Pt-PVP NPs annealed at 400°C have been chosen to perform preliminary gas sensing tests with CO and H₂ as described in the experimental section. The sensing response has been weak, but substantial if considered that the layers used had a thickness of 28 nm. Figure 6a reports the calculated Transmittance Change Ratio ($TCR = (T_{gas} - T_{air}) / T_{air}$) values for a TiO₂-Au thin layer containing only Au-PVP NPs annealed at 400°C. The transmittance variation is small in the low wavelength range, while it is more evident in the 550 - 650 nm SPR band region. The perturbation is similar after exposure to both gases, and in each case it is confined especially in the SPR region. When only Pt NPs are present in the film, the TCR trend is that of figure 6b. No perturbation is here obviously noticed in the 550 - 650 nm range, as no Au NPs are here present and Pt is known to have plasmonic resonance frequencies in the UV region [24]. No apparent features are noticeable in this plot. Figure 6c reports as a final comparison the TCR values calculated exposing a thin TiO₂ film containing both Au-PVP and Pt-PVP NPs to 1000 ppm of CO and H₂. Effect of Pt could be observed in the higher TCR values observed in the 350-550 nm range, a region in which sensitivity toward CO detection appears higher. Being the calculated values in such small range (optical transmittance variation in the -0.1 - 0.3% range) it would be premature to define an actual optical sensing effect of the Pt NPs.

Figure 6. Transmittance Change Ratio ($TCR = \frac{T_{\text{gas}} - T_{\text{air}}}{T_{\text{air}}}$) plots for TiO₂-Au, b) TiO₂-Pt, c) TiO₂-Au-Pt samples annealed at 400°C exposed to 1000ppm CO and H₂ at 300°C operative temperature.

As far as the Au SPR spectral region, Pt NPs do not seem to give any improvement on the actual response, but again since the sample thickness is so small, a definite assumption cannot be made. Sensor function tests performed on thicker samples would definitely give a more recognizable trend of values.

4. CONCLUSIONS

Au and Pt nanoparticles have been synthesized with colloidal techniques and used to dope TiO₂ sol-gel solutions. Thin films of pure TiO₂ and TiO₂ doped with Au and/or Pt have been prepared, and a study on the influence of annealing temperature and dopant presence on the optical and structural properties of the films has been presented. Both noble metals colloids are stable in the sol-gel solution environment, and no aggregation or segregation phenomena can be envisaged during deposition and annealing processes. Preliminary results on gas sensing tests are presented as one of the possible applications, which lie in other several fields of science and technology.

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