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Structural study of sol–gel Au/TiO_2 films from nanopowders

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ABSTRACT

TiO_2 represents one of the most important sol–gel materials, due to its photocatalytic properties, in the case of both powders and coatings. Nanostructured titania has been reported to be used in many applications in different fields ranging from optics to gas sensor via solar energy. Recent researches point out the existence of new procedures used in order to enhance the efficiency of the photocatalytic process. The metal ion doping is such an example. Two types of 2 wt.% Au containing TiO_2 powders have been embedded in sol–gel vitreous TiO_2 matrices. Au-doped TiO_2 films have been prepared from these sols, by dipping procedure using quartz microscopic slides, as substrates. The relationship between the synthesis conditions and the properties of titania nanosized materials, such as thermal stability, phase composition, crystallinity, and the influence of dopant was investigated. The hydrophilic properties of the films were correlated with their structure, composition and surface morphology.

1. Introduction

Chemical methods, such as sol–gel process, provide an attractive route for the preparation of nanocomposite thin films, homogeneous and with good adherence to the support. TiO_2 represents one of the most important sol–gel materials, due to its photocatalytic properties, in the case of both powders and coatings. Nanostructured titania films possess an immense range of applications, e.g. in the field of optics, electrical insulation, photovoltaic solar cells, electrochromic displays, antibacterial coatings, photocatalytic reactors, high performance anodes in ion batteries, and for gas sensing [1]. They are preferred for environmental protection due to their high ratio surface/volume, taking into account that photocatalytic process is based on the chemical reactions at the surface of the material. In order to enhance the efficiency of the photocatalytic process, the metal ion doping is applied. The study of Au-doped TiO_2 nanomaterials for photocatalytic applications became an interesting topic for research [2–9]. Recent investigations on gold titania nanocomposite particles show that metal ion doping extended the response of the photocatalyst into visible region. The catalytic properties of Au based materials depend on the support, on the preparation method and particularly on the shape and size of the Au clusters [4]. The noble metals, such as gold and platinum are capable to produce the highest Schottky barrier among the metals facilitating the electron capture [2,6]. In the present work, Au-doped sol–gel TiO_2 nanopowders have been embedded in vitreous TiO_2 matrices and the corresponding coatings have been prepared. Their structural study has been completed by hydrophilicity tests.

2. Experimental

Sol–gel Au/TiO_2 films from nanopowders have been obtained by the dipping procedure, using quartz microscopic slides, as substrates. Two types of Au containing TiO_2 powders have been embedded in the TiO_2 matrix, after the aging of the sol. They have been prepared using ultrasonically and microwave assisted hydrothermal synthesis (samples U and M, respectively). Both samples contained 2 wt.% dopant proceeding from hexachloroauric acid ($HAuCl_4$) and they were prepared as previously described [10]. The TiO_2 matrix was directly obtained from tetraethylorthotitanate (Merck), $Ti(OC_2H_5)_4$, using absolute ethanol (Riedel de Haën), as solvent, water for hydrolysis and nitric acid as catalyst. A very rigorous pH and viscosity control of the TiO_2 sol was necessary in order to establish the most propitious moment for including the nanopowder. The preparation of Au-doped TiO_2 films from nanopowders has followed the same flowchart as in the case of Pd-doped TiO_2 coatings previously prepared [11].

The obtained films have been dried at room temperature and then densified by thermal treatment at 300, 400 and 500 °C for 1 h,

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according to DTA/TGA results, using in all cases the same heating rate of 1 °C min^{-1}. The films were noticed GU and GM, depending on the nature of the embedded powder. The index corresponding to the temperature of thermal treatment was added. Thus, the samples were named as GU3–GU5 and GM3–GM5, respectively, while the un-doped films were labeled as TiO_2-M3–TiO_2-M5. In order to compare their structural behavior with the TiO_2 matrix the same thermal schedules have been applied.

The thermal and crystallization behaviors of the prepared samples were followed by thermal analysis, using a Mettler Toledo Star System TGA/SDTA851/LF 1600 °C apparatus. The structural evolution was studied by the X-ray diffraction with a Shimadzu XRD 6000 diffractometer, using Ni-filtered CuK_α radiation (λ = 1.5418 Å). The surface morphology of the films has been studied by atomic force microscopy (AFM) in non-contact mode. An OCA 15 EC (Data Physics Instruments) was used in the study of TiO_2 film hydrophilicity. The contact angle (CA) measurements between a drop of deionized water (500 nL) and the film surface were performed at room temperature, under 70% environment humidity conditions. A Hamilton motorized syringe (500 μL), operated by a computer, allowed the drop volume control. The samples were irradiated for photo-activation using filtered UV light (100 mW/cm^2, photon energy: 3.18–3.65 eV) from a high-pressure mercury lamp (150 W). The CA versus the UV irradiation dose was monitored until the surface photoactivation reached the saturation. Then CA values were measured during the back-reaction regime, with UV irradiation removed, every 9 h, in 7 time steps, keeping the samples in a dark place between measurements.

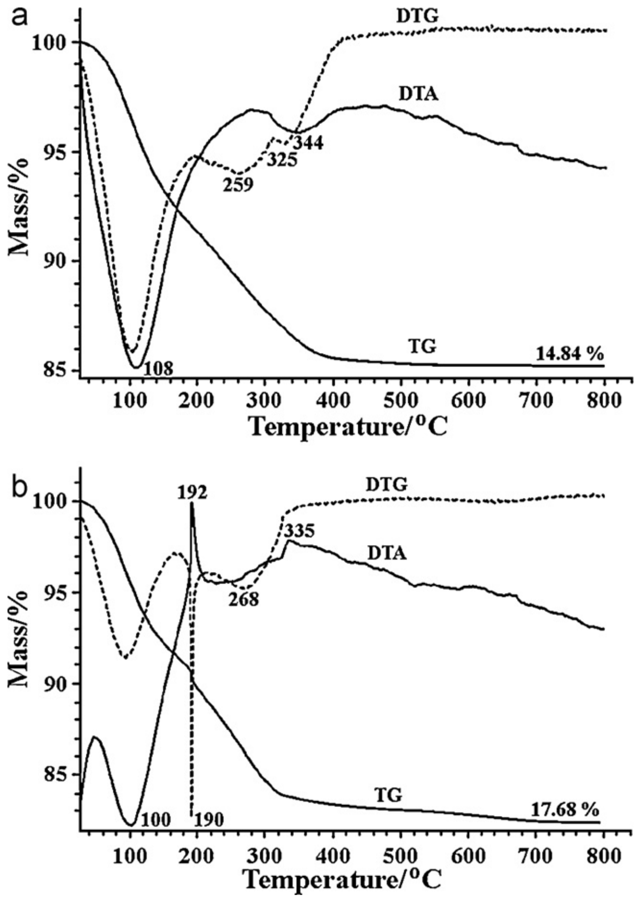

Fig. 1. Thermal behavior of GM (a) and GU gel coatings (b).

3. Results and discussion

In the experimental conditions mentioned in Section 2, continuous and homogeneous coatings with good adherence to the support were obtained. The thermal processing of the films was determined taking into account the thermal behavior of the gels obtained from the gelation of the sols used for coating preparation. DTA/TGA results of the Au/TiO_2 gel coatings (GM and GU) are presented in Fig. 1.

DTA curves show an intense endothermic effect at ~100 °C, due to adsorbed water and alcohol removal associated with mass losses on TG curves. Another endothermic effect at ~260 °C can be seen for both samples, due to the decomposition of the organic matter. For the GM sample, a supplementary small endothermic effect at 325 °C can be noticed. For the GU sample, two exothermic effects at 192 and 335 °C are observed, the first one correlated with mass loss and the second one without mass loss, probably due to TiO_2 anatase crystallization.

Structural evolution with temperature of the Au/TiO_2 gel coatings obtained from nanopowders, compared with the pure TiO_2 one (TiO_2-M), in the same range of temperature (300–500 °C), is presented in Table 1. The experimental data were obtained from computerized analysis of XRD spectra with a proper XRAY5.0 program [12].

The evolution of the normalized microstructural factors, for anatase phase, was represented as histograms (Fig. 2) in which: $\langle\delta UCV\rangle$ represents the difference between the volumes of the elemental cells, $\langle D\rangle$ is the mean value of the crystallite size, and $\langle S\rangle$ signifies the average value of the tensile strain. For the un-doped sample, TiO_2-M, with the increase of the temperature, a decrease of the internal strain concomitant with the increase of the crystallite size was noticed. The increase of the rate of crystallite growth with temperature is significantly diminished for the samples belonging to the GM3–GM5 series, compared to the GU3–GU5 one. For the GM3–GM5 samples the variation of UCV follows almost precisely the tensile strain evolution, while in the GU3–GU5 case, a progressive decrease of the UCV with the increase of temperature can be observed. The worst case regarding the structural disorder for both series of prepared materials refers to sample GU4. In this case, the profile analysis finds the lowest value of the mean crystallites size, corresponding to the highest average tensile strain. For samples thermally treated at 400 and 500 °C, the dopant presence induces greater internal strain.

For all series of samples (TiO_2-M3–TiO_2-M5, GU3–GU5 and GM3–GM5, respectively) the rutile phase has been detected only at 500 °C. Fig. 3 presents the corresponding histograms.

An ideal correlation between the tensile strain variation and the crystallite size has been observed: the crystalline order is present at short distances for higher strains. In the same time, the UCV of the rutile phase from the GM5 sample seems to suffer a contraction, compared to sample GU5. The presence of the dopant generates greater internal strain.

From Fig. 4 it can be observed that the contact angle decreases with the increase of the UV-irradiation dose, but not all the samples became super-hydrophilic (CA values below 10° [13]). In fact, only the films thermally treated at 400 °C, namely GM4 and GU4, reach CA values of 4.0° and 6.0° respectively. They are followed by GU5 sample, which still presents good hydrophilic properties (CA of 13.0 for a saturated surface photoactivation). For the mentioned samples, it is worth noting that the CA decreases rapidly, the surface photoactivation reaching the saturation for an UV dose of about 12 J/cm^2. When keeping these samples in darkness, the recovery of the initial contact angle values occurs after time intervals larger then 43 h (Fig. 5), depending on the sample structure and surface condition. Of note especially GM4 and GU4 samples which maintain their super-hydrophilicity for 18 h. The same pictures show that the other three samples have worse hydrophilic properties.