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Article

Sol-gel Synthesis and Antioxidant Properties of Yttrium Oxide Nanocrystallites Incorporating P-123

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Abstract: Yttrium oxide (Y_2O_3) nanocrystallites were synthesized by mean of sol-gel method using two different precursors. Raw materials used are yttrium nitrate and yttrium chloride, in methanol. In order to promote oxygen vacancies, P123 poloxamer was incorporated. Synthesis systems were heat-treated at temperatures from 700 ºC to 900 ºC. Systems at 900 ºC were prepared in the presence and absence of P123 using different molar ratios (P123:Y, 1:1, 2:1). Infrared Spectroscopy results revealed characteristic absorption band of Y-O vibrations typical of Y_2O_3 matrix. Structural phase was analyzed trough X-ray Diffraction, showing the characteristic cubic phase in all systems. The diffraction peak that presented the major intensity corresponded to the sample prepared from yttrium chloride incorporating P123 in a molar ratio of P123:Y, 2:1 at 900 ºC. Crystallites sizes were determined by Scherrer equation, having them from 21 to 32 nm. Antioxidant properties were estimated by DPPH• assays; the results are presented and discussed.

Keywords: Yttrium oxide; nanocrystallites; sol-gel; antioxidant properties.

1. Introduction

Nowadays, nanoscience and nanotechnology have a variety of practical applications in which the elaboration of nanosystems and the synthesis of nanostructured materials are a major trend. Since nanotechnology deals with materials or structures in nanometer scales, typically ranging from subnanometers to several hundred nanometers and it is well known that that the properties are not the same in a nanometer scale than those observed for bulk materials, it has been a aim to produce highly specialized new systems. Nanomaterials are present in different areas as electronic, automotive, construction, biomaterials, and many others. For biomaterials applications, there are many different classes such as polymers, metallic alloys, ceramics, etc. Commonly, ceramic materials are inorganic, non-metallic materials prepared from compounds including a metal and a non-metal material, and may be crystalline or partially crystalline [1]. The final uses of ceramic nanomaterials are varied, depending on their synthesis process, chemical composition, and final presentation (nanoparticles, films, etc). For example, the so-called bioceramics can be used in biology and medicine fields, which are designed to elicit a specific physiological behavior and to be used in living organisms [2]. Thus, nanoparticles prepared from some metal oxides have shown potential scavenger behavior and in particular, yttrium oxide is nowadays considered an important compound due to its high free energy to oxide formation from elemental yttrium among known metal oxides [3]. It is known that CeO_2 and NiO nanoparticles are relatively nontoxic to neutrophiles and macrophages, therefore, these particles protect cells from death due to oxidative stress, and the protection is due to the direct antioxidant properties of nanoparticles. Yttrium oxide presents the same typical cubic structure of cerium oxide, so it can be considered a candidate for biological applications; so, it is considered that yttrium oxide may act as a free radical scavenger. This metal oxide is characterized by only small deviations from stoichiometry under normal conditions of temperature and pressure and by absorption of water and carbon dioxide from the atmosphere [3]. Yttrium oxide has been prepared by several synthesis methods as liquid-phase reaction [4], polyol [5], spray pyrolysis [6], homogeneous precipitation [7] and sol-gel [8,9]. The sol-gel method has emerged as one of the most promising processes due to its unique advantages such as high chemical homogeneity, capacity to achieve several compositions and ability to prepare preferential crystal structures. In this paper, we report the structural and antioxidant properties of Y_2O_3 prepared by sol-gel method using two different precursors and including P-123 poloxamer. Crystal structural characterization was carried out by X-Ray diffraction (XRD). Infrared Spectroscopy (FT-IR) studies were conducted to study the evolution of organic-inorganic compounds. Antioxidant properties were evaluated using DPPH assays. There are no studies about Y_2O_3 using P-123 poloxamer nanoparticles produced by sol-gel method and its antioxidant properties.

2. Results and Discussion

Yttrium oxide materials were prepared at different synthesis conditions, as described in experimental section. Summary of prepared systems used in this paper is presented in Table 1.

Table 1. Y_2O_3 systems prepared by sol-gel method, key words and general description.

Sample	Precursor	Matrix	Poloxamer	P-123:Y Molar ratio	T / ºC	Crystallite size / (nm)
Y1	$Y(NO_3)_3$	Y_2O_3	-	-	700	26
Y2					800	27
Y3					900	26
Y4	YCl_3		-	-	700	32
Y5					800	29
Y6					900	29
Y9	$Y(NO_3)_3$		P-123	1:1	900	21
Y10				2:1	900	28
Y11	YCl_3		P-123	1:1	900	29
Y12				2:1	900	29

2.1. Chemical and structural characterization

Typical infrared absorption bands of Y_2O_3 synthesized from yttrium nitrate and chloride precursors were analyzed by mean of Infrared spectroscopy (FT-IR) studies. Systems prepared from addition of P-123 poloxamer into the synthesis process and heat-treated at different temperatures were also analyzed. In Figure 1, Y1-Y12 systems IR spectra are presented. For samples Y1 and Y2 it is observed an absorption band corresponding to oxygen-metal around 500 and 600 cm^{-1} as reported for yttrium oxide when it is prepared by sol-gel method [10]. In samples Y3-Y12 we observe absorption bands associated to coordinated water (δH_2O), therefore it can be linked to asymmetric vibration bands corresponding to COO^- from air and atmosphere humidity [11].

Figure 1. IR spectra of Y_2O_3 systems heat-treated from 700 to 900 °C.

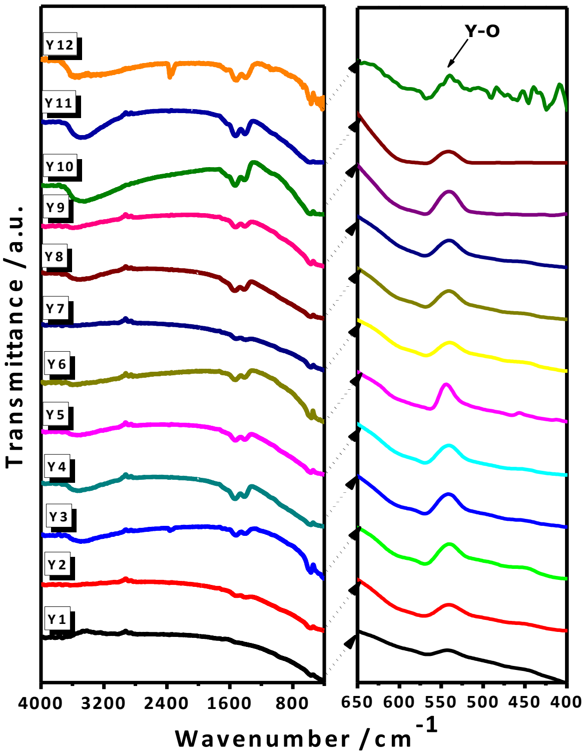


Figure 2. XRD patterns of Y_2O_3 systems heat-treated from 700 to 900 °C.

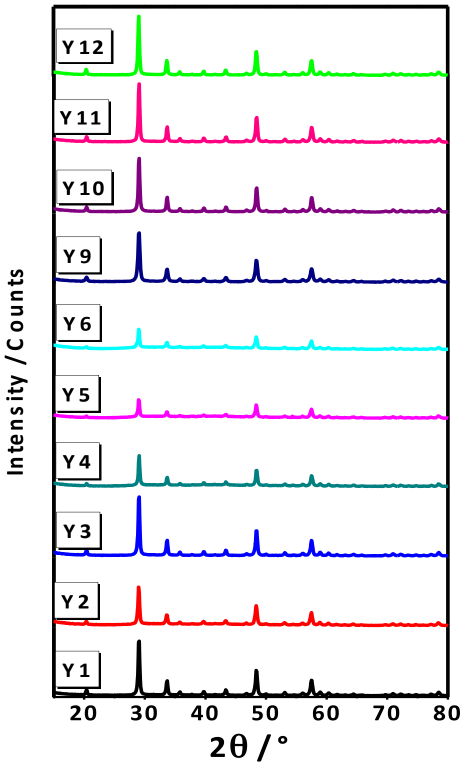


Figure 3. XRD patterns of Y_2O_3 systems prepared from yttrium nitrate and yttrium chloride at different temperatures.

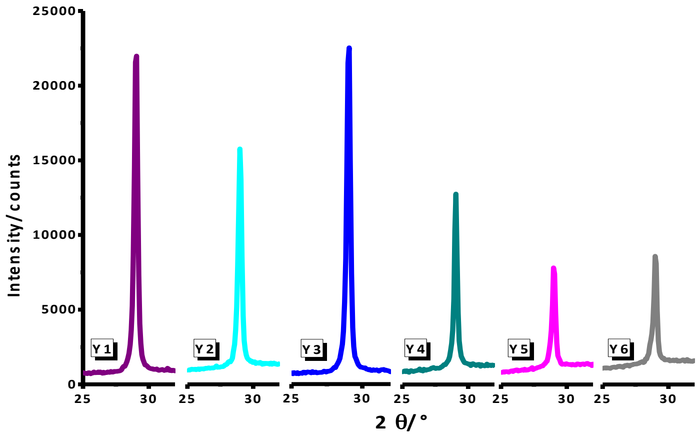


Figure 4. XRD pattern of Y_2O_3 powder synthesized from yttrium nitrate in the presence and absence of P-123 poloxamer heat-treated at 900 °C for 1 hour.

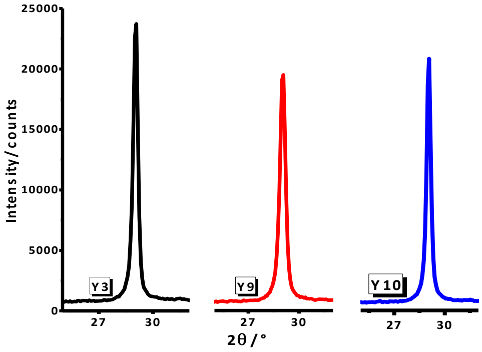
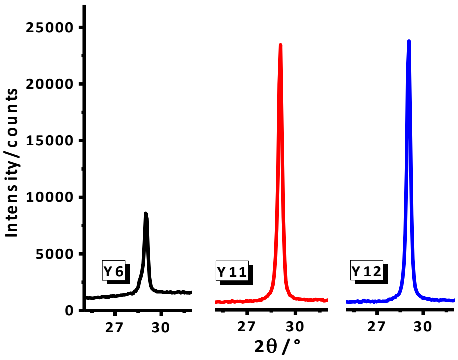
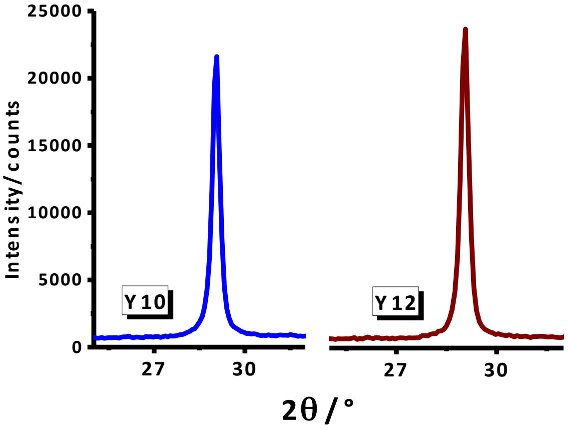


Figure 5. XRD pattern of Y_2O_3 powder synthesized from yttrium chloride in the presence and absence of P-123 poloxamer heat-treated at 900 °C for 1 hour.



In order to determine the crystalline structure of the yttrium oxide powders from yttrium nitrate and yttrium chloride precursors and systems prepared using P-123 poloxamer, heat-treated from 700 ºC to 900 ºC for 1 hour, X-ray diffraction analysis was carried out. XRD profiles of Y_2O_3 powders for each synthesis procedure are shown in Figure 2 (Y1-Y12). As it can be observed, no secondary phases are found within the detection limit of XRD technique. It can be noticed that the cubic structure of Y_2O_3 is formed at 700 ºC and it remains stable until 900 ºC [PDF cart 201412]. Synthesized samples from yttrium nitrate (Y1-Y3) showed a greater degree of crystallization compared with those synthesized from yttrium chloride (Y4-Y6), X-ray diffraction patterns are presented in Figure 3. A comparison in crystallization degrees between systems prepared from yttrium nitrate and those prepared from yttrium chloride in the presence and absence of P-123 poloxamer is presented in Figure 4 and 5 respectively. The XRD results showed that yttrium oxide systems embedded in P-123 poloxamer in a molar ratio of P-123:Y; 2:1 have better crystallization degree as is shown in Figure 6. The crystallite sizes were determined by mean of Scherrer equation. Table 1 shows the sizes, in a range between 21 to 32 nanometers.

Figure 6. XRD pattern of Y_2O_3 powder synthesized from yttrium nitrate and yttrium chloride using P-123 poloxamer in a molar ratio of P-123:Y, 2:1.



2.2. Antioxidant assays

The DPPH• without nanoparticles does not reveal changes in absorption characteristic peak (Figure 7). Antioxidant properties for yttrium oxide samples Y1-Y12 were tested. Graphic for sample Y12 that showed the best antioxidant behavior of all synthesized compounds is presented in figure 8. It can be observed that DPPH• diminishing begins at 5 min and it is evident after 60 min. It is known that the antioxidant property may be due to the neutralization of DPPH• free radical character, explained by electron transference from the reactant [12].

3. Experimental Section

3.1 Synthesis procedure

Yttrium oxide was prepared by sol-gel method according the following procedure. All experiments were carried out at room temperature. Experimental strategies for yttrium oxide powder preparation used two raw materials: yttrium nitrate and yttrium chloride. For yttrium oxide synthesis hexa-hydrate yttrium nitrate [Sigma-Aldrich, $Y(NO_3)_3$•$6H_2O$, 99.8 %], hexa-hydrate yttrium chloride [Alfa Aesar, YCl_3•xH_2O, 99.99 %], methanol [Sigma-Aldrich, CH_3OH, 99.8 % (MeOH)], acetylacetone [Sigma Aldrich, $CH_3COCH_2COCH_3$, 99.9 % (AcAc)], and for embedded system P-123 poloxamer [Sigma-Aldrich, $(C_3H_6O$•$C_2H_4O)x$, PM:~ 5800] were used. 0.0026 mol of $Y(NO_3)_3$•$6H_2O$ or 0.0051 mol of YCl_3•xH_2O were dissolved in MeOH in a molar ratio of MeOH/Y=123 under vigorous magnetically stirring for 15 min. Thereafter, AcAc was added in order to obtain stable sol of Y_2O_3. In selected systems P-123 poloxamer was incorporated in a molar ratio described in Table 1. Yttrium oxide xerogel was formed at 90 ºC for 24 hours. Finally, different heat-treatments were carried out in order to produce dense materials and to promote the crystallization of the yttrium oxide powder at 270 °C (2 h), 500 °C, 700 °C, 800 °C and 900 °C for 1 h.

Figure 7. Time dependent of DPPH• scavenging in the absence of nanocrystals.

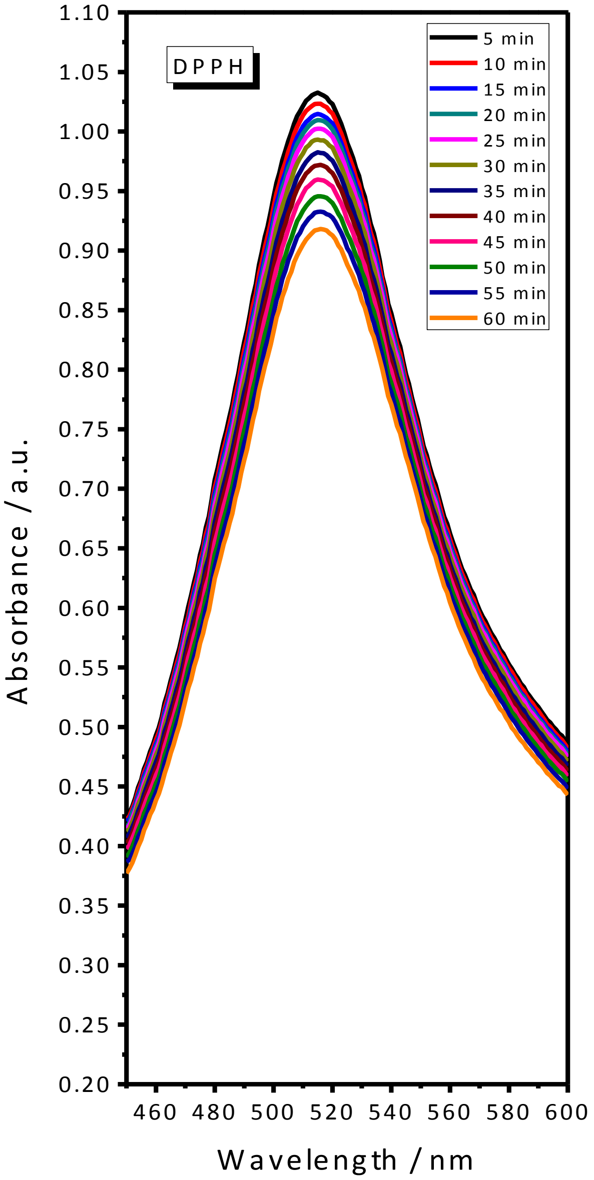
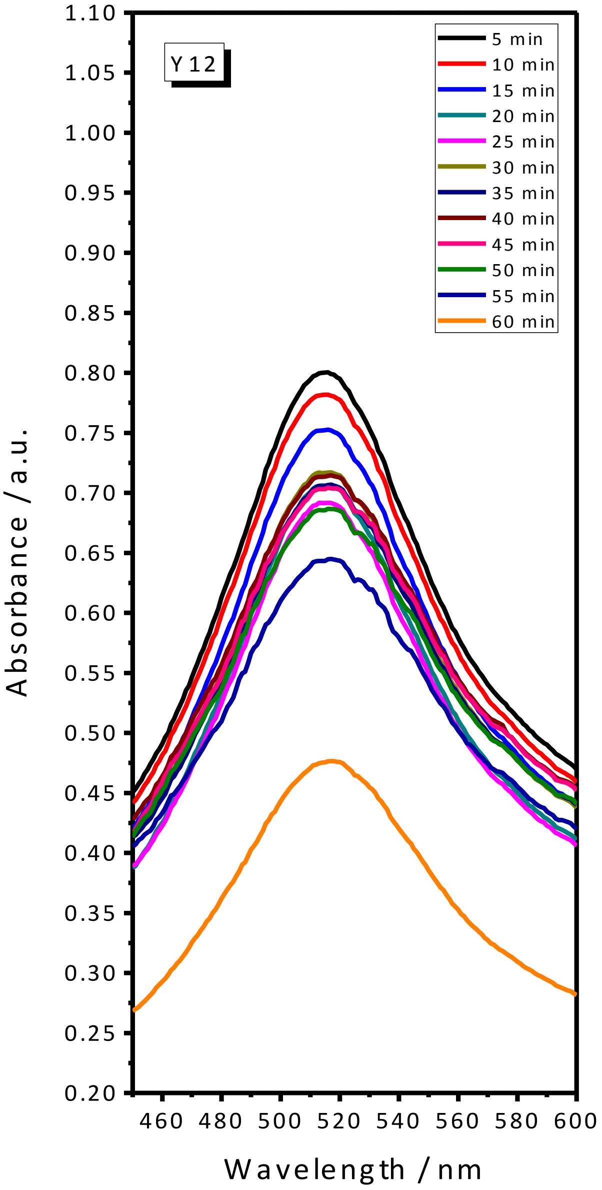


Figure 8. Time dependent of DPPH• scavenging in the presence of yttrium oxide nanocrystallites (sample Y12).



3.2 Apparatus

The IR transmittance spectra were recorded from yttrium oxide powders heat-treated at different temperatures using a Bruker Tensor 27 model in a range of 4000-400 cm^{-1}. Samples were analyzed using KBr pelleting technique (4.0 cm^{-1} resolution, 15 scans, 15 seconds). The structure was determined by a Bruker diffractometer D8 Advance using a cooper anticathode at 35 kV and 25 mA in a range 2θ from 15 to 80°. The crystallite size was determined according to Scherrer equation, considering the line broadening of the diffraction peak due to the effect of crystal size [13]:

$$\beta = \frac{\kappa * \lambda}{\mathrm{FWHM} * \mathrm{Cos}\theta}$$

Where β is the crystallite size of the powder, κ the factor shape of the crystal, λ (0.15406 nm) is light wavelength, FWHM is the full-width at half-maximum of the peak, and θ is the Bragg angle of X-ray diffraction peak.

4. Conclusions

Yttrium oxide nanocrystallites were successfully synthesized by sol-gel method from yttrium nitrate and yttrium chloride as precursors. Yttrium oxide nanostructured powders prepared from yttrium chloride and in presence of P-123 poloxamer in a molar ratio of P-123:Y 2:1 presented better physicochemical properties (crystallinity and purity) that systems prepared from yttrium nitrate precursor. Yttrium oxide powders were presented a range of 21 to 32 nanometers of crystallite size. The DPPH studies are reported for the first time for yttrium oxide synthesized by sol-gel method, so there is no reference to compare. Yttrium oxide nanocrystallites show enhanced antioxidant properties, therefore they can be considered as new promising materials in biological systems.

Acknowledgments

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Conflicts of Interest

The authors declare no conflict of interest.

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