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QUANTUM DOT BASED ON TIN/TITANIUM MIXED OXIDE DOPED WITH EUROPIUM SYNTHESIZED BY PROTEIN SOL-GEL METHOD

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ABSTRACT

Special luminescence biomarkers have been developed to find more sensitive fluoroimmunoassay methods. A new generation of these biomarkers is the semiconductors nanocrystals, known as quantum dots, doped with lanthanides. The use of lanthanides ions as luminescent markers has many advantages, for example a security method, low cost, high specificity and also the luminescence can be promptly measured with high sensibility and accuracy. The protein sol-gel is a modification of conventional method, in which the coconut water replacing the alkoxides normally used. The advantage is that, the proteins present in coconut water bind chemically with metal salts forming a polymer chain. This work presents nanoparticles based on tin/titanium mixed oxide doped with 3% of europium synthesized by protein sol-gel method. The nanoparticles were burned at 300ºC, 500ºC, 800ºC and 1100ºC. The samples were analyzed and characterized by thermal analysis, X-ray powder diffraction (XRD), infrared spectroscopy (IR) and scanning electron microscopy (SEM). The synthesis was effective and the nanoparticles showed nanometric size and structural differences with the annealing. To be used in the fluoroimmunoassays tests, these particles need to be functionalize before be connect with biological molecules and after this process, these nanoparticles going to be submitted at gamma radiation for sterilization.

1. INTRODUCTION

Biomolecular assays are used in the study of functions and methods as ultra-sensitive detection of biological species, responsible for numerous diseases. A generation of biomarkers is semiconductor nanocrystals (quantum dots) that are functionalized for recognition of the biomolecules. These nanocrystals are doped with lanthanide to have the luminescent answer with high sensitivity and accuracy [1].

The protein sol-gel process was discovered in 1998 and has been used in the nanostructured oxides synthesis [2-6]. It is a sol-gel process modified that coconut water is used in place of conventional alkoxides [7].

The coconut water has a complex chemical composition. It is basically composed by sugar, minerals and small quantities of lipids and nitrogen compounds.
The sol-gel with coconut water is formed when metallic salts (chlorides, nitrates and sulfides) are chemically bonded to the proteins, which are present in coconut water forming a polymer

chain. The proteins are formed by amino acids chains which have amine (NH_2) and carboxylic acid (COOH) groups responsible by metal complexation.

Amino acids have compatibles properties with sol-gel process needs; because they are soluble in water, react with base and acid to form organic salts (amphoteric character), they are not volatile and suffer polymerization reaction. The main amino acid presents in coconut water is alanine which has negative charge from the oxygen atoms and it can bind to the metal cation. The nitrogen present in amino acid has a pair of free electrons that can receive H^+ ion of the carboxylic acid and then the alanine acquires a positive and negative terminal, enabling solvate cations and anions [7].

Due coconut water to be composed for several proteins and fats it has not been clearly understood how protein sol-gel is formed or stabilized. The most likely is the bind chemically of the metal with the proteins, because when a salt is dissolved in proteins, the stability time increases by 50 times. The presence of metal ion prevents the proteins decomposed and leads to formation of fungi and bacteria [8].

The main advantages to use coconut water as molecular precursor are: low toxicity compared to conventional alkoxides; abundance; low cost and simplicity production. Besides that has the characteristic of decreasing particle size [9]. However, the coconut water has minerals salts dissolved and it nature and concentration can change according to the source and degree maturity of the coconut. So, the challenge of the technique is to determine the influence of the impurities in the physical proprieties of prepared material. [3, 5-7].

2. EXPERIMENTAL SECTION

We adapted our method based on protein sol-gel synthesis process develop by Macedo [9-12]. The mixed oxide $SnO_2/TiO_2:Eu^{3+}$ was prepared by neutralization of a mixing solution of tin (IV) chloride, titanium (IV) chloride, europium chloride and coconut water with ammonia solution, until pH7, in a batch reactor. The particles were aged in the solution liquor for 48h. The precipitated was washed with water and to analytical control of chloride ions it was made a test with $AgNO_3$. After removal of chloride ions, the material was burned at 300, 500, 800 and 1100 °C for 1 hour 300°C and 500°C and 2hours for 800°C and 1100°C.

The mixed oxide was characterized by: X-ray diffraction obtained in MiniFlex II Rigaku X-ray diffraction by using CuKα radiation with 2θ from 5° to 80º; Infrared spectra obtained in an absorption spectrometer Thermo Scientific Nicolet 6700 FT-IR, Smart Orbit Diamond 30.000 to 200 cm^{-1}, Class1 laser product; Scanning electron microscopy using a Philips model XR-30 by the technique of "spputering"; Thermal analysis where TG curves were obtained in a Thermal balance SDTA-822 (Mettler Toledo) using samples with approximately 10 mg in alumina crucible under a dynamic atmosphere of nitrogen, flow rate of 50 mL min^{-1}, and a heating rate of 10 °C min^{-1}. The DTG curves were obtained from electronic differentiation of the TGA signal.

3. RESULTS AND DISCUSSIONS

3.1 Syntheses mixed oxide

The mixed oxide $SnO_2/TiO_2:Eu^{3+}$ synthesized was doped with 3%mol of europium concerning to the molar amount of tin. The obtained material was dark and rigid at 300°C however when the temperature of annealing increase the properties of this material change and it becomes less rigid and the color exchange to white (Fig. 1).

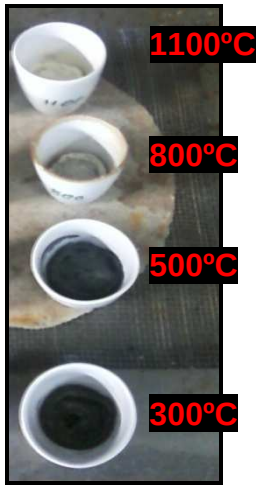

Figure 1. $SnO_2/TiO_2:Eu^{3+}$ annealed at 300 ºC, 500 ºC, 800 ºC and 1100 ºC.

3.2 X-Ray Powder Diffraction

The fig. 2 show the diffractograms of $SnO_2/TiO_2:Eu^{3+}$ with different annealing temperature (300 °C, 500 °C, 800 °C and 1100 °C). They present fine peaks suggesting a crystalline structure. The majority phases are casseterite and anatase to the mixed oxide ($TiO_{0.1}$ $Sn_{O.9}$ O_2) ICCD 01-070-4411 (~26,7 (1,1,0); ~34,5 (1,0,1); ~51,5 (2,1,1); ~65,0 (3,1,0)). The peaks approximately 2θ: 28; 40; 50 and 67 do not appear in the diffractogram of material annealed at 1100 °C, on the other hand for the material annealed at 300 °C the lines at 2θ: 26; 34; 52; 55; 58; 59; 62; 65; 66; 71; 79 vanish, suggesting different structural phases with annealing treatment (first phase for 300 °C, second phase to 500 °C and 800 °C and third phase to 1100 °C).

To study the influence of the annealing temperature in the size of crystallite it was plotted the average of crystalline size against annealing temperature (Fig 3). We can observed an increase in the crystallite size with the temperature, until 800 °C, but when the phase change starts, at 1100 °C , the crystallite size average decrease.

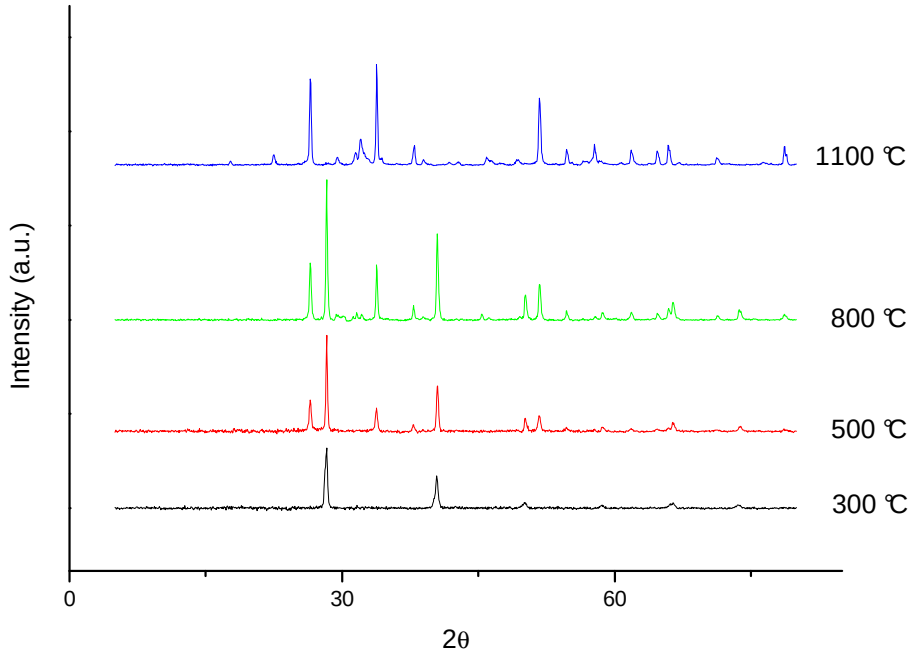

Figure 2. X-ray powder diffraction of $SnO_2/TiO_2:Eu^{3+}$ annealed at 300 ºC, 500 ºC, 800 ºC and 1100 ºC.

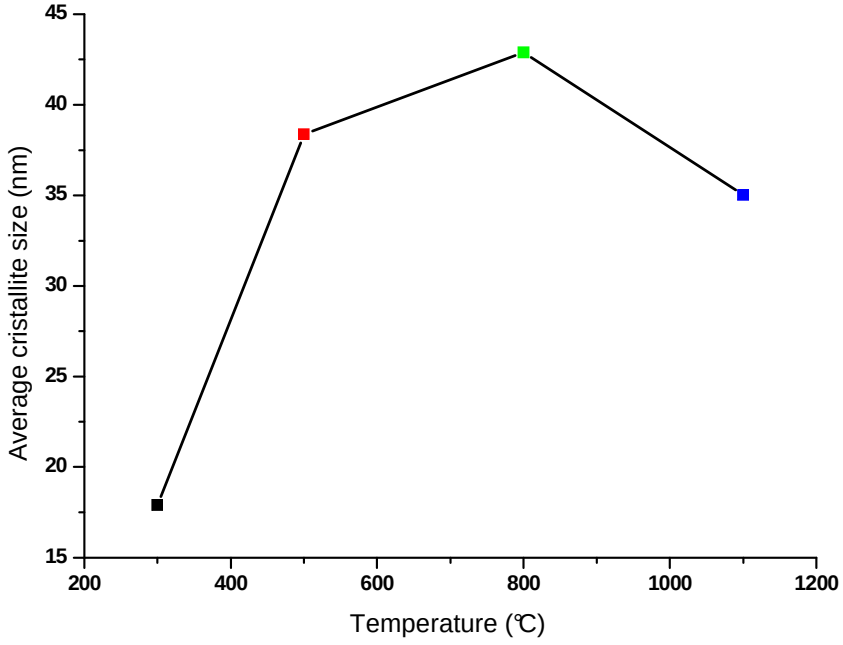

Figure 3. Crystalline size plotted against annealing temperature for $SnO_2/TiO_2:Eu^{3+}$.

3.3 Infrared Spectroscopy

Fig. 4 represents the infrared spectra to Ti/Sn mixed oxide in different annealing temperature. The large band in the region 3530-2390 cm^{-1} were attributed to stretch νOH to water and hydroxyls binding different metals [13, 14]. The band in ~1630 cm^{-1} was attributed to angular deformation δH–O–H and the strong band in ~1426 cm^{-1} to deformation CH_2 [15]. Barraclough et al. [16] studied alkoxides infrared spectra to some metals (aluminum, titanium, zirconium, hafnium, niobium e tantalum) and tried attributed to ν(C–O)M and ν(M–O) bands and derivatives. Based on this studies it was conclude that the bands in region 800–1100 cm^{-1} were attributed to ν(C–O)M and the other that appear at ~1020 cm^{-1} was attributed to stretch νSn-O [13].

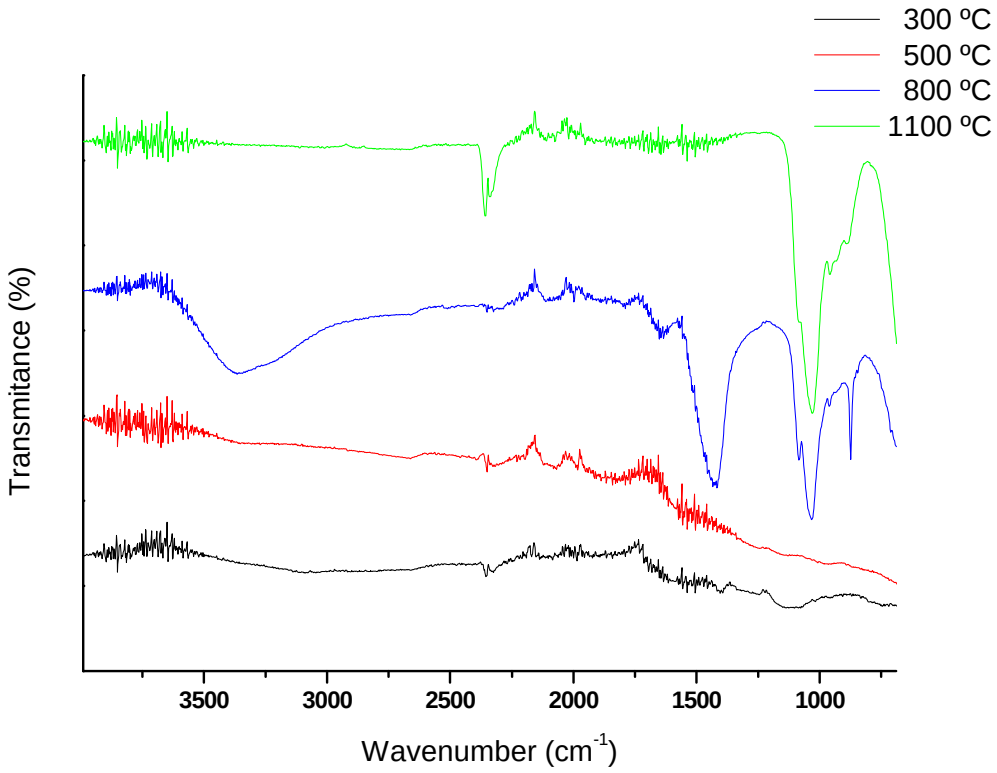

Figure 4. Infrared spectra to different annealing

3.4 Scanning electron microscopy

The SEM micrographies (Fig 5) was made for the samples annealed to different temperatures magnified until 2500X to 300°C and 500°C and 1000X to 800°C and 1100 °C. The micrographs (Fig. 5) showed different morphology, with homogeneous surfaces clusters that acquire more crystalline appearance as the annealing temperature increases.

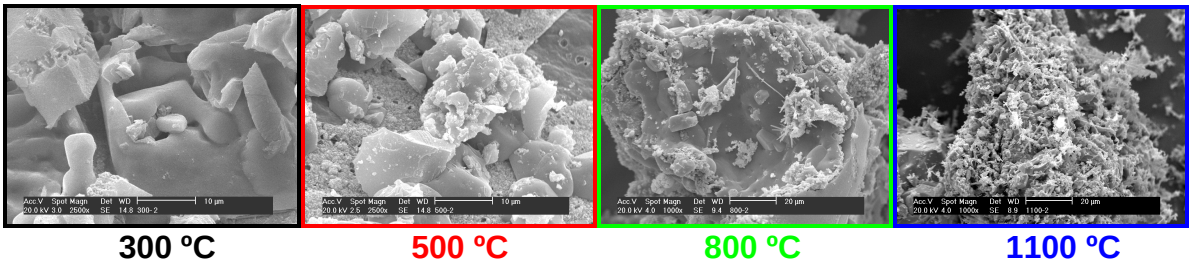

Figure 5. Micrographs to different temperature annealing with zoom 2500X (300°C and 500 °C) and 1000X (800°C and 1100 °C)

3.5 Thermal Analysis

Fig. 6 show TG and DTG curves to $SnO_2/TiO_2:Eu^{3+}$ obtained by protein sol-gel process, where it is observed five events of mass loss : 83 – 151 ºC (21.11%), 144 – 262 ºC (31.95%) attributed to dehydration and crystallization water loss, 234 – 392ºC (12.46%) attributed to hydroxyl loss [17-20] and the events with peaks at 640 ºC and 1000 ºC are attributed to phase transitions as showed by X-ray diffraction data.

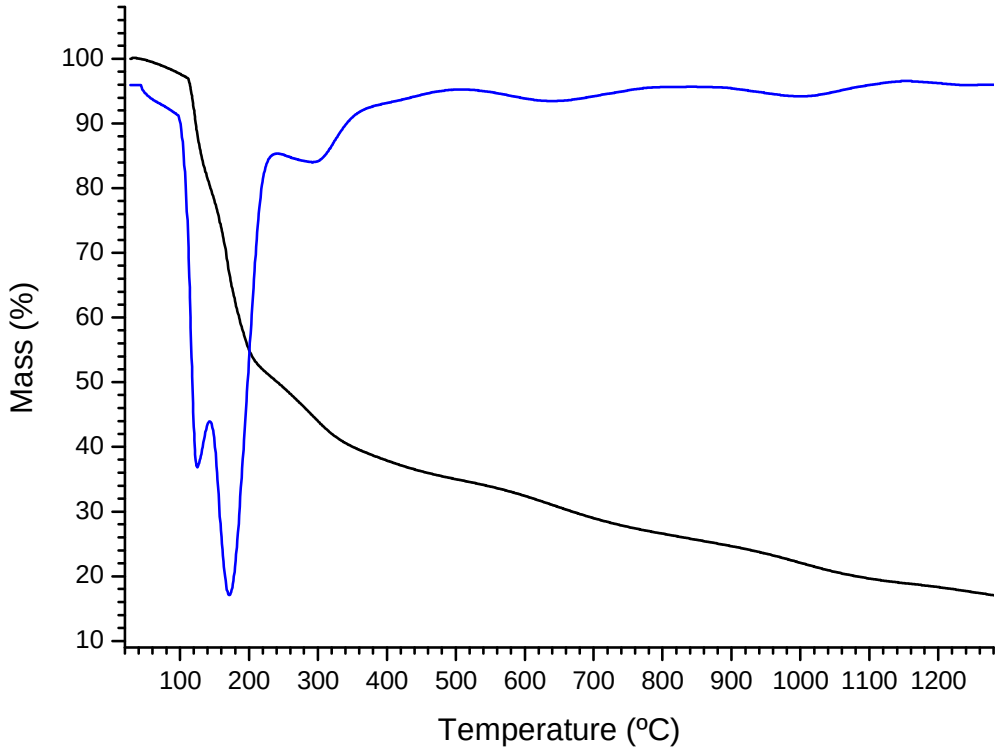

Figure 6. TG and DTG curves to $SnO_2/TiO_2:Eu^{3+}$

4. CONCLUSIONS

The syntheses of mixed oxide, $SnO_2/TiO_2:Eu^{+3}$, by protein sol-gel method was effective and showed structural differences according to annealing temperature. The casseterite and anatase phase were the majority phases however it could observe three phase changes and homogeneous surfaces clusters with different crystallinity. From that and also analyzing the infrared it is possible to conclude that until 500 °C the organic phase was predominant and above this temperature, it could be observe the real structure of the marker. The next step is the functionalization of nanoparticles and sterilization with gamma radiation.

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