

## SYNTHESIS AND MORPHOLOGICAL CHARACTERIZATION OF NANOCOMPOSITE BASED ON ANODIC TiO<sub>2</sub> NANOTUBES AND POLY(N-MALEOYL GLYCINE-CO-ACRYLIC ACID)

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### ABSTRACT

In this study, we examined the synthesis, and characterization of TiO<sub>2</sub>/poly(N-maleoylglycine-co-acrylic acid) (TiO<sub>2</sub>/poly(MG-co-AA)) nanocomposite. The nanocomposite was prepared by the dispersion of TiO<sub>2</sub> nanotubes in a water solution of the polymer (3% w/w) and then it was lyophilized. The nanocomposite was characterized by FTIR and Raman spectroscopies. The incorporation of TiO<sub>2</sub> nanotubes to the polymeric matrix was determined by transmission electron microscopy (TEM) from which TiO<sub>2</sub> nanotubes in the inner of copolymer with diameters ranging between 90 and 100 nm were observed. The overall morphology of the previously synthesized nanotubes was determined by scanning electron microscopy (SEM). For the nanocomposite system, the morphology was studied by atomic force microscopy (AFM) from which a grain shape structure was observed. This process resulted in a new nanocomposite material with an average grain diameter estimated by SEM and AFM ranging between 210-240 nm. It was observed that the nanotubes were homogeneously dispersed within the polymeric matrix. The prepared material could be suitable in the design of electronic devices and additionally could have potential applications as biomaterial.

**Keywords:** polymer nanocomposite, morphological characterization, TiO<sub>2</sub> nanotubes.

### 1. INTRODUCTION

The continuous technological advancement demands the design of structures with specific characteristics so as to meet the needs of various innovative applications. A promising alternative source to solve this problem is the compound material synthesis. Besides, if the goal is the search of miniaturization of these devices at a nanometric size, it is highly possible to obtain materials with unique properties, generally known as nanocomposites. The properties of these nanostructured compounds are affected by either their size or the functionality of the specific chemical species within and/or outer of them.

The nanocomposites of our interest are shaped according to modifications of tubular nanostructures of titanium dioxide (TiO<sub>2</sub>-Nt)<sup>1-7</sup> through their adding in water soluble copolymeric systems (derived from polymaleoyl glycine (p[MG])<sup>8-10</sup>).

Inside nanomaterials, the titanium dioxide nanotubes have been one of the most studied compounds in the literature<sup>2-4</sup>. Additionally, it is a well-known fact that we can obtain highly organized TiO<sub>2</sub>-Nt structures, which can be generated under different anodization conditions. Historically, the titanium oxide doped with different metals has been carried out with the aim of improving the conducting properties of this material; as for example, preventing the process of recombination of electron-hole pair without losing the integrity of its crystalline structure<sup>5,6</sup>. Besides, the titanium oxide nanostructure modification can increase the versatility of its properties with the objective of searching for new applications. Lastly, the integration at a nanometric scale of organic and inorganic materials for their use in living organisms, such as: cells, virus and bacteria, is positively being used in the emerging field of nanomedicine nowadays<sup>11,12</sup>.

The use of organic materials, e.g. polymers, to stabilize and produce metallic oxide nanostructures has drawn the attention of the scientific world since they are a highly viable prospect for new technological applications. The confinement of polymers, in its topography or chemistry, has effectively been used to control the distribution and orientation during the formation and/or incorporation process of metal oxide structures inside the polymeric matrix<sup>13,14</sup>.

In the current research work, we report the synthesis and morphological characterization of TiO<sub>2</sub>/poly(maleoylglycine-co-hydroxyethylmetacrylate) nanocomposite. The nanocomposite preparation was effectively done by titanium oxide nanotube dispersion in an aqueous solution of the copolymer. The chemical characterization was successfully carried out by FT-IR and Raman spectroscopies; and the morphological one, by atomic force microscopy

(AFM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). All in all, the research results show that this innovative material has potential applications as biomaterial, and additionally, for new electronic device design.

### 2. EXPERIMENTAL

#### Synthesis of poly(MG-co-AA)

Poly(N-maleoyl glycine-co-acrylic acid), P(MG-co-AA) was synthesized by radical copolymerization with a 1:1 feed monomer composition in solution using 0.5 mol% of AIBN as the initiator as was previously reported<sup>15</sup>.

#### Synthesis of TiO<sub>2</sub> nanotubes

The anodization of titanium was performed as previously reported<sup>16</sup> by applying a step voltage  $U_a = 60V$  in a 0.2 % w/w ammonium fluoride, 3 % v/v water in ethylene glycol electrolyte with continuous stirring at 20 °C. TiO<sub>2</sub> nanotubes synthesized in ethylene glycol electrolytic medium were dispersed by sonication in 10 mL of deionized water, then filtered on Millipore PVDF syringe filters (pore diameter 200 nm). The filtrates were then lyophilized in a freeze Christ model Alpha 1-2 plus.

#### Preparation of TiO<sub>2</sub>/poly(MG-co-AA) nanocomposite

The formation of the TiO<sub>2</sub>/poly(MG-co-AA) nanocomposite was accomplished by the sonication at 130 Hz of frequency aqueous dispersions of TiO<sub>2</sub> nanotubes (Fig. 1) in 10 mL of deionized water. Containing the copolymer (3% w/w). The suspension containing the TiO<sub>2</sub>/poly(MG-co-AA) was lyophilized to obtain the solid nanocomposite.

#### Characterization

Infrared spectrum was recorded on a Perkin Elmer FTIR spectrum Two and an UATR Two accessory was used in measurements of the samples in the solid state.

Raman experiments were performed ex situ (in air) using a Horiba LabRAM HR spectrometer, employing an Ar laser (514.5 nm wavelength).

The surface morphology of the nanocomposite system was characterized by scanning electron microscopy (SEM) using a Carl Zeiss Sigma model microscope and AFM using Nanionics Multi View MV1000. In AFM measurements, n-type silicon cantilevers (tip radius ≈ 20 nm;  $f = 39.4$  kHz;  $Q = 1576$ ) for intermittent mode were employed. Transmission electron microscopy (TEM) was performed using a LEO 1420VP equipment. For TEM measurements, an aqueous dispersion of TiO<sub>2</sub>/poly(MG-co-AA) nanocomposite obtained by sonication of the films in isopropyl alcohol during 15 min was employed. The analysis of obtained images was performed with the image processing software Gwyddion 2.37.

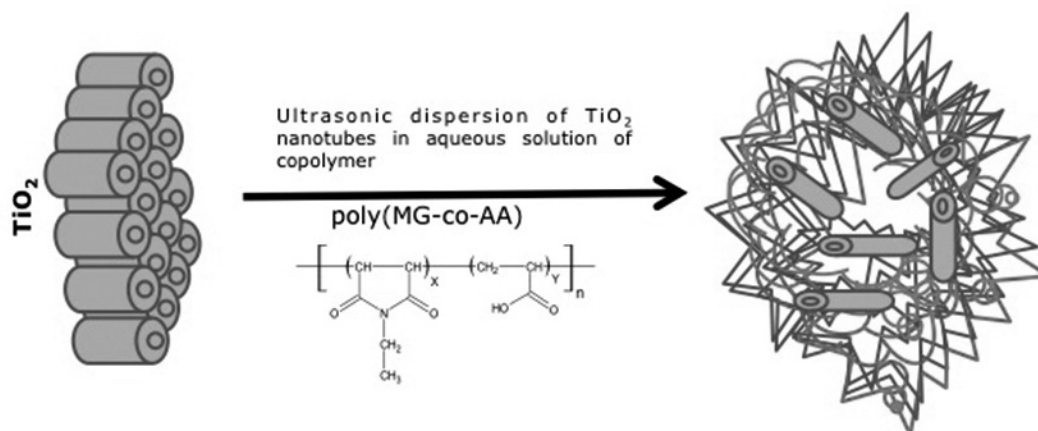


Figure 1. Schematic representation of preparation  $\text{TiO}_2/\text{poly}(\text{MG-co-AA})$  nanocomposite.

### 3. RESULTS AND DISCUSSION

#### 3.1 Chemical and morphological characterization

The FT-IR spectra of the poly(MG-co-AA) and  $\text{TiO}_2/\text{poly}(\text{MG-co-AA})$  are presented, in Figure 2. The FT-IR spectrum of the poly(MG-co-AA) (Figure 2.a) show the characteristic absorption bands of the stretching of C=O in the acrylic acid at 1695, stretching of the N-C of the imide ring at 1424. The FT-IR spectra of the nanocomposite system are given in Fig. 2b. A slight change in the intensity of the C=O signal at 1695  $\text{cm}^{-1}$  was observed, due to the interaction of  $\text{TiO}_2$  with the carboxylate groups of the polymer.

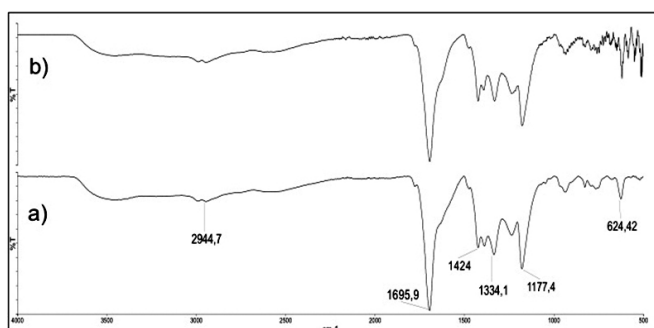


Figure 2. FTIR spectra of the poly(N-maleoyl glycine-co-acrylic acid) copolymer (a) and  $\text{TiO}_2/\text{poly}(\text{N-maleoyl glycine-co-acrylic acid})$  nanocomposite (b).

With the purpose of further studying the molecular interactions between the copolymer and the  $\text{TiO}_2$  surface, the Raman spectra for the solid poly(MG-co-AA), the  $\text{TiO}_2$  nanoporous surface and the  $\text{TiO}_2/\text{poly}(\text{MG-co-AA})$  nanocomposite were recorded. For the copolymer (Fig. 3a), mainly the (N-C stretching of imide ring) characteristic vibrations are obtained, namely the ring breathing at 321.1  $\text{cm}^{-1}$ ; the C-C-H in-plane bend at 365  $\text{cm}^{-1}$ ; the C-C inter-ring stretching at 518  $\text{cm}^{-1}$ ; respectively<sup>10</sup>. For  $\text{TiO}_2$ -Nt films (Fig. 3b), the presence of broad bands at 187; 464 and 606  $\text{cm}^{-1}$  and the absence of well-defined signals corresponding to anatase (144; 399; 515 and 640  $\text{cm}^{-1}$ ) or rutile (240; 447 and 612  $\text{cm}^{-1}$ ) crystalline phases, indicated that the anodic films obtained are amorphous<sup>17</sup>. Raman spectra for  $\text{TiO}_2/\text{poly}(\text{MG-co-AA})$  nanocomposite are shown in Figure 3c. In these spectrum an overlapping of the signals, in the range of 50-600  $\text{cm}^{-1}$ , was observed indicating the presence of both species. Additionally a new signal was recorded at 819  $\text{cm}^{-1}$  and it was attributed to the interaction between the copolymer and  $\text{TiO}_2$  nanotubes.

The resulted surface morphology of the  $\text{TiO}_2$  nanotubes films was analyzed by SEM (Fig. 4a) and for  $\text{TiO}_2/\text{poly}(\text{MG-co-AA})$  nanocomposite by SEM, AFM and TEM techniques (Figs. 4 (b-c)). Average measurements

of the nanotubes give values of diameter of  $90 \pm 8$  nm and 11  $\mu\text{m}$  of length<sup>18</sup>. The surface of nanocomposite films presented a granular structure with an average size ranging between 212 and 275 nm as can be seen in the images 2D AFM and SEM micrographs, Figure 4(b-c), AFM images of the film show a uniform granular surface morphology due to agglomeration of the copolymer around the  $\text{TiO}_2$  nanotubes. Figure 4c corresponds to the TEM micrograph, showing the results of both bright and dark fields respectively which confirmed the incorporation of  $\text{TiO}_2$  nanotubes embedded into the polymeric material. Additionally, the distribution of individual nanotubes was observed from the TEM measurements of the  $\text{TiO}_2/\text{poly}(\text{MG-co-AA})$  (Figure 4 c). TEM image allows determining whether the nanotubes are occluded within the copolymer or if this effect is due to surface roughness. For this reason a measurement was performed in the dark field TEM mode (Fig. 4 c bottom), from which semiconductor materials are observed as bright spots<sup>19</sup>. The bright tubes correspond to  $\text{TiO}_2$  nanotubes with approximate diameters ranging between 90 and 100 nm.

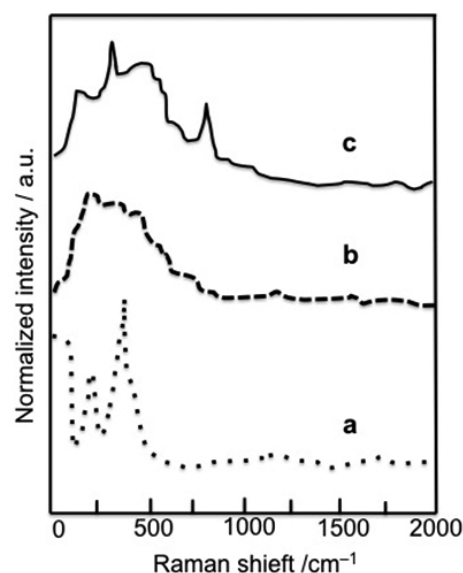
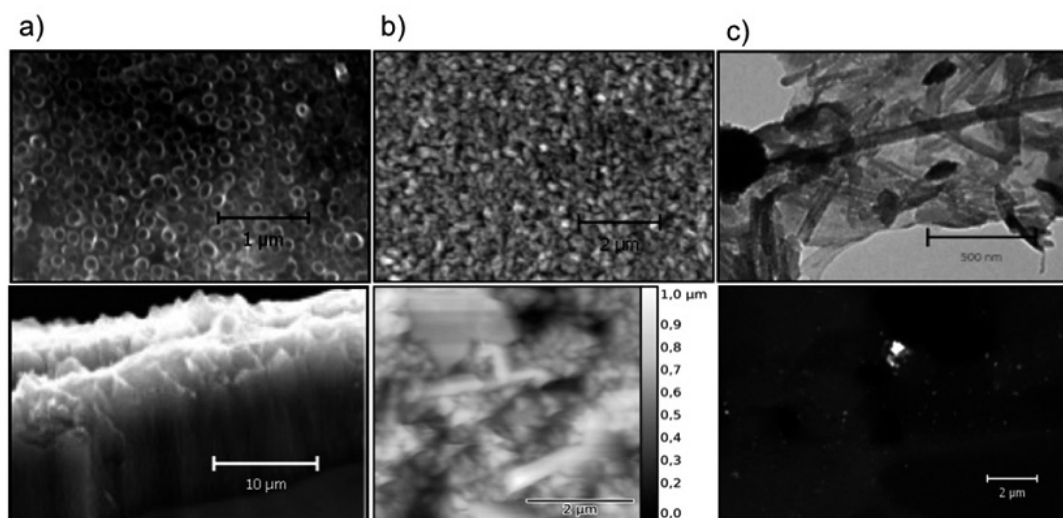


Figure 3. RAMAN spectra of solid poly(MG-co-AA) (a),  $\text{TiO}_2$  nanotubes (b), and  $\text{TiO}_2/\text{poly}(\text{MG-co-AA})$  nanocomposite (c).



**Figure 4.** a) SEM images of the TiO<sub>2</sub> nanotubes films (up and lateral view). b) SEM and 2D AFM of TiO<sub>2</sub>/poly(MG-co-AA)] c) TEM and dark-field TEM images of TiO<sub>2</sub>/poly(MG-co-AA)].

#### 4. CONCLUSIONS

This work has described the preparation of TiO<sub>2</sub>/poly(MG-co-AA)] nanocomposite via incorporation of TiO<sub>2</sub> nanotubes into of interpolymeric matrix by chemical techniques in aqueous solution. This process resulted in a new nanocomposite material with an average grain diameter ranging between 210-240 nm. The nanotubes were homogeneously dispersed in the polymeric matrix. It was possible to observe to the surface morphology of the nanocomposite material by SEM and AFM techniques, and their morphology was attributed to the copolymer composition, as well as to their interaction with the nanotubes, however TiO<sub>2</sub> nanotubes could not be observed on the surface. The characterization of the surface morphology by SEM and AFM shows a homogeneous surface covered by copolymer beads with an approximately diameter of 220 nm. Furthermore, TEM and dark field TEM mode microscopy provided reliable measurements from which a bright spots that corresponds to TiO<sub>2</sub> nanotubes in the inner of copolymer with diameters ranging between 90 and 100 nm were observed.

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