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SYNTHESIS AND MORPHOLOGICAL CHARACTERIZATION OF NANOCOMPOSITE BASED ON ANODIC TiO_2 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_2/poly(N-maleoylglycine-co-acrylic acid) (TiO_2/poly(MG-co-AA)) nanocomposite. The nanocomposite was prepared by the dispersion of TiO_2 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_2 nanotubes to the polymeric matrix was determined by transmission electron microscopy (TEM) from which TiO_2 nanotubes in the inner of copolymer with diameters ranging between 90 and 100 nm were observed. The overall morphology of the previously synthetized 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 nanocompsite 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_2 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_2-Nt)[1-7] through their adding in water soluble copolymeric systems (derived from polymaleoyl glycine (p[MG]) [8-10].

Inside nanomaterials, the titanium dioxide nanotubes have been one of the most studied compounds in the literature [2-4]. Additionally, it is a well-known fact that we can obtain highly organized TiO_2-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 [5, 6]. 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 [11, 12].

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 [13, 14].

In the current research work, we report the synthesis and morphological characterization of TiO_2/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 [15].

Synthesis of TiO_2 nanotubes

The anodization of titanium was performed as previously reported [16] by applying a step voltage Ua = 60V in a 0.2 % w/w ammonium fluoride, 3 % v/v water in ethylene glycol electrolyte with continuous stirring at 20 °C. TiO_2 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_2/poly(MG-co-AA) nanocomposite

The formation of the TiO_2/poly(MG-co-AA) nanocomposite was accomplished by the sonication at 130 Hz of frequency aqueous dispersions of TiO_2 nanotubes (Fig. 1) in 10 mL of deionized water. Containing the copolymer (3% w/w). The suspension containing the TiO_2/ 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 Σigma 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_2/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.

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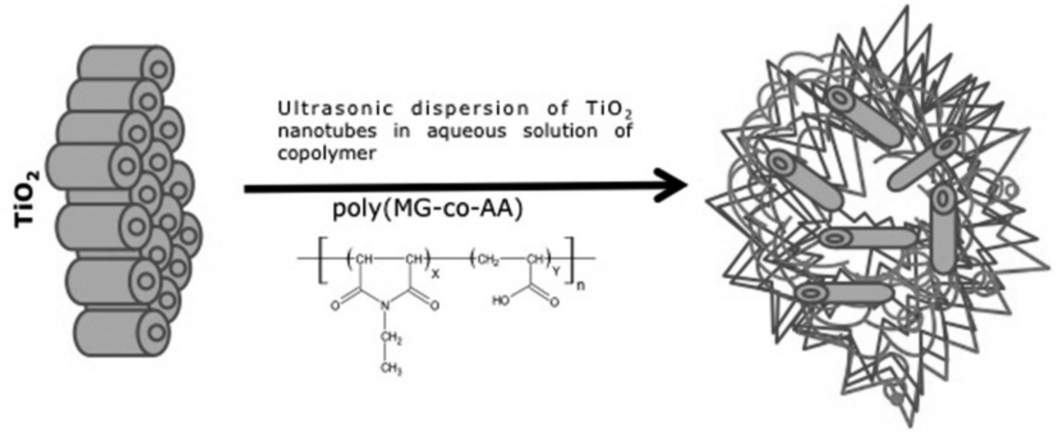

Figure 1. Schematic representation of preparation TiO_2/poly(MG-co-AA) nanocomposite.

3. RESULTS AND DISCUSSION

3.1 Chemical and morphological characterization

The FT-IR spectra of the poly(MG-co-AA) and TiO_2/poly(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 cm^{-1} was observed, due to the interaction of TiO_2 with the carboxylate groups of the polymer.

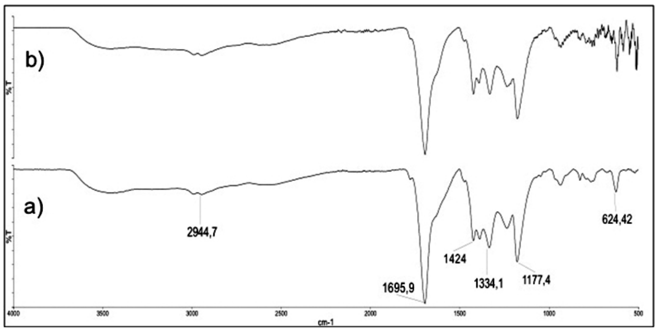

Figure 2. FTIR spectra of the poly(N-maleoyl glycine-co-acrylic acid) copolymer (a) and TiO_2/poly(N-maleyl glycine-co-acrylic acid) nanocomposite (b).

With the purpose of further studying the molecular interactions between the copolymer and the TiO_2 surface, the Raman spectra for the solid poly(MG-co-AA), the TiO_2 nanoporous surface and the TiO_2/poly(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 cm^{-1}; the C-C-H in-plane bend at 365 cm^{-1}; the C-C inter-ring stretching at 518 cm^{-1}; respectively [10]. For TiO_2-Nt films (Fig. 3b), the presence of broad bands at 187; 464 and 606 cm^{-1} and the absence of well-defined signals corresponding to anatase (144; 399; 515 and 640 cm^{-1}) or rutile (240; 447 and 612 cm^{-1}) crystalline phases, indicated that the anodic films obtained are amorphous [17]. Raman spectra for TiO_2/poly(MG-co-AA) nanocomposite are shown in Figure 3c. In these spectrum an overlapping of the signals, in the range of 50-600 cm–1, was observed indicating the presence of both species Additionally a new signal was recorded at 819 cm^{-1} and it was attributed to the interaction between the copolymer and TiO_2 nanotubes.

The resulted surface morphology of the TiO_2 nanotubes films was analyzed by SEM (Fig. 4a) and for TiO_2/poly(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±8 nm and 11 µm of length [18]. 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 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 TiO_2 nanotubes embedded into the polymeric material. Additionally, the distribution of individual nanotubes was observed from the TEM measurements of the TiO_2/poly(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 [19]. The bright tubes correspond to TiO_2 nanotubes with approximate diameters ranging between 90 and 100 nm.

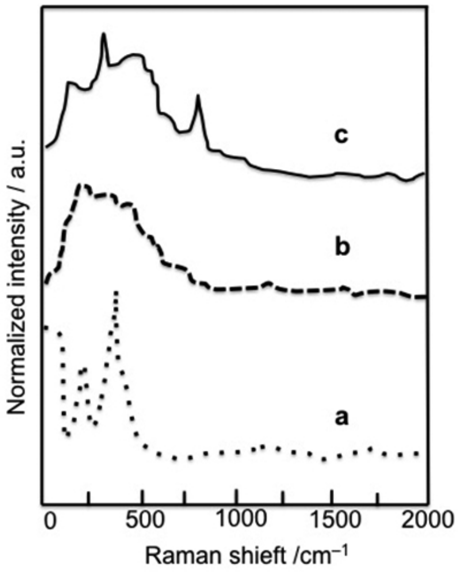

Figure 3. RAMAN spectra of solid poly(MG-co-AA) (a), TiO_2 nanotubes (b), and TiO_2/poly(MG-co-AA)] nanocomposite (c).

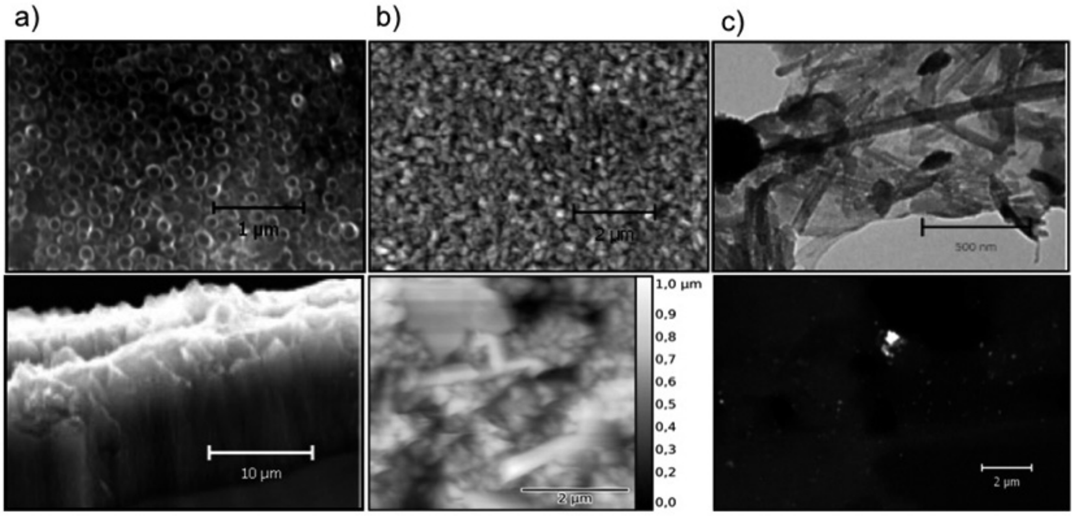

Figure 4. a) SEM images of the TiO_2 nanotubes films (up and lateral view). b) SEM and 2D AFM of TiO_2/poly(MG-co-AA)] c) TEM and dark–field TEM images of TiO_2/poly(MG-co-AA)].

4. CONCLUSIONS

This work has described the preparation of TiO_2/poly(MG-co-AA)] nanocomposite via incorporation of TiO_2 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_2 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_2 nanotubes in the inner of copolymer with diameters ranging between 90 and 100 nm were observed.

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