Materials Letters 174 (2016) 95–98

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Novel simple method for preparing tailored polymer-titania nanotubes hybrid materials

Javier Marugán [a,b,*], Cintia Casado [a,b], Gregory Silverberg [b], Chad D. Vecitis [b]

[a] Department of Chemical and Environmental Technology (ESCET), Universidad Rey Juan Carlos, C/ Tulipán s/n, 28933 Móstoles, Madrid, Spain
[b] School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, United States

ARTICLE INFO

Article history:
Received 13 December 2015
Received in revised form
10 March 2016
Accepted 11 March 2016
Available online 15 March 2016

Keywords:
Titania nanotube
Polymer
Membrane
Hybrid material
Anodization

ABSTRACT

A novel method for preparing hybrid polymer-titania nanotube (TNT) arrays with promising optical, catalytic and filtration applications is reported. The procedure is based on a one-step rapid galvanostatic anodization followed by the transfer of the TNT arrays to a polymer support by applying heat and pressure. The fraction of open-ended tubes can be controlled by changing the intensity of the current at the end of the anodization step. For example, completely open-ended or close-ended TNT arrays can be obtained by applying high or low current intensity, respectively at the end of the anodization process. The reported procedure allows the one-step simple and rapid preparation of flexible hybrid polymer-TNT materials which have great potential for photonic flow-through membranes.

1. Introduction

Titania nanotube (TNT) attracts significant research interest due to their interesting optical and catalytic properties that have promising potential applications in solar cells [1], fuel cells [2], chemical sensors [3], water splitting [4,5] photocatalytic processes [6,7] and biomedical applications [8,9]. From the different methods reported in the literature to prepare TNT-based materials [10], the electrochemical anodization of titanium has been extensively studied as a method to form highly ordered arrays of TNT. Since the electrochemical growth of TNT by anodization of titanium in fluoride containing electrolytes was first reported by Zwilling and co-workers [11], researchers have focused on understanding the mechanism of the process [12], the effect of the process variables on the morphological parameters of the synthesized TNT [13], the effect of the metal alloy composition [14] and the comparison between potentiostatic and galvanostatic conditions [15]. Incorporation of TNT to plastics has also been reported by anodization of a previously deposited titanium thin layer [3,16] (bottom closed TNT) or by incorporating hydrothermally synthesized TNT (disordered) to polymer membranes [2,17].

Preparation of flow-through TiO_2 nanotube arrays have been reported to be possible by different procedures [18], including the decrease [19] or the increase [20] of the voltage at the end of a two-step potentiostatic anodization process. In this work, a novel simple method for preparing polymer-TNT arrays hybrid materials using a one-step rapid galvanostatic method is reported. A fine tune of the current and time at the end of the anodization step allow the control of the tube opening process, leading to tailored materials with completely open or close-ended TNT that can be successfully transferred to flexible polymer substrates by applying heat and pressure.

2. Material and methods

TNT arrays were prepared by anodization of titanium foils (Trinity Brand Industries Grade 2 #6T-5, thickness 0.005 in.) in an ethylene glycol electrolyte containing 0.15 M NH_4F (Sigma-Aldrich, > 98%) and 5 wt% deionized water. Prior to the treatment, titanium pieces were degreased by ultra-sonication in ethanol for 15 min and covered with Scotch tape to frame 4 cm^2 of exposed surface. Anodization was carried out in a stirred 100 mL volume two-electrode cell using a 4 × 6 cm stainless steel sheet as counter electrode placed in a centered position regarding the anode at a distance of 2 cm. The cell was immersed in an ice bath to keep temperature at 0 °C even when applying high intensity currents. An Agilent Technologies N5750A System DC Power Supply with maximum values of 150 V and 5 A was used to carry out the

* Corresponding author at: Department of Chemical and Environmental Technology (ESCET), Universidad Rey Juan Carlos, C/ Tulipán s/n, 28933 Móstoles, Madrid, Spain.
E-mail address: javier.marugan@urjc.es (J. Marugán).

http://dx.doi.org/10.1016/j.matlet.2016.03.054
0167-577X/

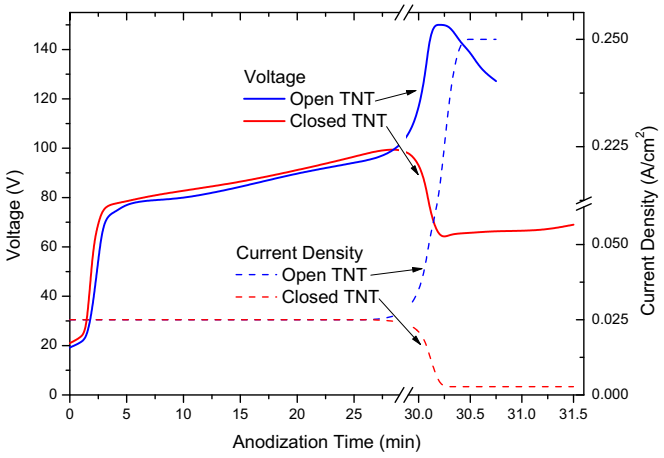

Fig. 1. Time profiles of current and voltage during the anodization of samples to obtain transferred arrays of closed and open TNT.

anodization under galvanostatic control at a current density value of 0.025 A/cm^2 for 30 min, followed by a final step of sudden increase or decrease of the current value.

Transfer of the TNT array to the polymer substrate (nylon membrane filters, 0.45 μm, 47 mm in diameter, Omicron Scientific 170047X) was conducted using a Carver bench top heated press model 4386. Optimal conditions for the transfer were found to be 20 bar, 55 °C and 30 min, although those values strongly depend on the polymer.

SEM images were obtained using a Zeiss Supra55VP FESEM at 5 kV with the inlens detector. Samples were previously coated with a 10 nm Pt/Pd conductive layer.

3. Results and discussion

Galvanostatic anodization of the titanium foil led to the rapid growth of a titania nanotube layer. Optimal conditions to form well-ordered TNT layers several microns in thickness were found to be 30 min at a current density of 0.025 A cm^{-2}. Higher currents leads to the formation of a nonhomogeneous layer and total corrosion of some areas of the titanium sheet, whereas shorter anodization times impact the ordered structure of the TNT arrays. Fig. 1 shows the evolution of the voltage and current density along the anodization process. Initially, a low potential (~20 V) is enough to keep the current density set point. A drastic increase in the voltage to values close to 80 V was observed after two minutes, because of the increase in the resistance due to formation of a compact TiO_2 layer. Subsequently, fluoride attack on the TiO_2 layer limits the global electrical resistance of the TNT layer, resulting in a slow linear potential increase to around 100 V during the remaining anodization time. As a result, the proposed galvanostatic anodization reduces significantly the required anodization time in comparison with the commonly reported potentiostatic formation of TNT.

Fig. 1 also shows the rapid change in the voltage and electrical current applied at the end of the process. A fast decrease in the anodization current allows the separation of closed TNT from the support whereas a fast increase in the current leads to the opening of the tubes, which will be discussed below.

Transfer of TNT to the polymer material is achieved by a hot press. Fig. 2 depicts the photographs of the TNT before and after transfer to the polymer membrane. The conditions for the transfer have to be carefully optimized depending on the polymer characteristics, such as glass transition temperature. The goal is getting the TNT anchored to fiber structure of the polymer without clogging the pores. In the case of the nylon membranes employed in this study, best results were obtained upon application of 20 bar and 55 °C for 30 min. Stronger conditions of temperature, pressure or time lead to the partial melting of the polymer with a significant reduction in the porosity. The use of methanol or other solvent to assist the detachment process is not recommended, as it prevents adhesion to the polymer.

SEM images of the prepared polymer-TNT hybrid materials are shown in Fig. 3. Fast reduction of the current density to 0.00275 A cm^{-2} during 90 s at the end of the anodization process led to TNT layers with closed tubes (Fig. 3a and b), On the other hand, a fast increase in the current density up to 0.25 A cm^{-2} for 30 s is enough to generate open-ended TNT (Fig. 3e and f) and weaken the anchorage of the TNT to the titanium foil. Longer times and/or higher intensities could lead to the loss of the TNT

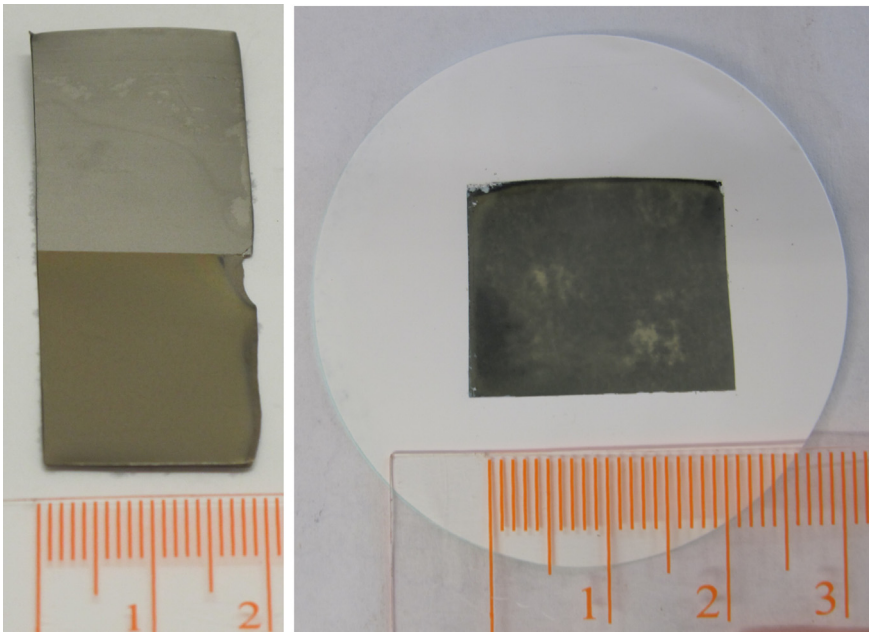

Fig. 2. Photograph of a TNT array before (left) and after (right) the transfer to the polymer.