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Three dimensional PEDOT nanowires network

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ABSTRACT

A three dimensional (3D) structure of poly(3,4-ethylenedioxythiophene) (PEDOT) nanowires have been prepared by electrochemical polymerization using 3D-alumina templates. The templates were synthesized by pulse anodization in an electrochemical bath. A 3D free standing network has been obtained after the template removal. The morphological analysis by electron microscopy shows the existence of a 3D PEDOT nanowires network whose nanowire diameter is around 20 nm for the vertical nanowires and 10 nm for the transversal connections. Electrical properties such as the *I–V* characteristics and the Seebeck coefficient were studied for the nanowires network. Also, the optical properties have been studied by Raman spectroscopy to confirm the creation of the PEDOT network. In summary, we have provided a very simple method to obtain three-dimensional nanostructures of conductive polymers. Any conductive polymer can be grown using our method.

1. Introduction

Currently, nanostructured materials have been the focus of many research works due to their special properties compared with bulk materials [1–4]. Scientific fields such as catalysis, biomedicine, optoelectronic and energy, have achieved a breakthrough in their respective areas using nanostructured materials during last tow decades. There are several methods to produce polymer nanostructures. The most commonly used are: electron beam lithography and optical lithography [5], soft template [4,6–8] and finally hard template [9,10]. The last two methods have become very important in the development of many strategies to nanostructure polymeric materials. Soft template methods are based on the employment of micelles formed by surfactants to confine the polymerization of conductive polymers into low dimensional materials. The typical synthesis is carried out in two different phases, both immiscible. This method includes micro-emulsion [6], mini-emulsion [7] and emulsion polymerization [8]. The hard template procedure uses a rigid material as a template to produce the nanostructures. Anodized alumina membranes are the most common material used as a rigid template, since it is very easy to control the thickness and the pore diameter thought the experimental conditions. This method allows manufacturing quasi-one-dimensional nanostructures such as nanotubes, nanowires and nanorods with a relatively low cost and high versatility in terms of diameter and length. Recently, the fabrication of a novel 3D alumina membranes by Caballero-Calero et al. [11] opened the gate to new three dimensional material networks in the nanoscale. The advantage of this method is the possibility to obtain a large area material (several cm^2) with a well-defined nanostructure. In the case of intrinsically conducting polymers (ICP), nanostructuration plays an important role. Usually, ICP are semiconductors and have been used in the development of many electronic devices such as solar cells [12], transistors [13], thermoelectric modules [14–16], organic light emitting diodes [17] and supercapacitors [18–20]. A well defined 3D network of nanowires can be the key in the next generation of electrodes for supercapacitors applications. These nanostructures provide a large number of advantages such as: 3D continuous electron pathway, the same mechanical robustness as its bulk counterpart or fast electron transfer into the 3D continuous framework [21]. In this work, 3D alumina membranes have been prepared by a combination of a soft and a hard anodization process. Then these alumina templates have been used, for the first time, for the synthesis of a 3D nanowires network of a conductive polymer, PEDOT.

2. Experimental

2.1. Materials

The reactants used in this work are: 3,4-ethylenedioxythiophene (EDOT), lithium perchlorate ($LiClO_4$), ethanol and acetonitrile. They were purchased from Sigma Aldrich. The aluminum foils (99.999%) were obtained from GoodFellow.

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2.2. Synthesis of the alumina membranes

The synthesis is based on two oxidative steps: firstly anodization and secondly a pulsed anodization [11]. This process allows controlling the nature of the morphology of the porous oxide layer on the aluminum depending of the experiential conditions. First for all the aluminum foil was subjected to several clean steps in an ultrasonic bath (5 min each step) using the following sequence of solvents: acetone, 1-propanol, water and ethanol. After the clean process the aluminum foil was electropolished at 20 V, 298 K with a high stirring during 3–5 min in $HClO_4$:ethanol (1:3). Then the first oxidization was carried out at 25 V, 274 K with low stirring during 24 h in a solution of H_2SO_4 0.3 M. To remove the first oxidization oxide layer a selective etching with CrO_3/H_3PO_4 aqueous solution has been made. After that, this aluminum foil was subjected to a pulse anodization process using the following experimental conditions: 25 V during 100 s and 32 V during 2 s, this sequence was repeated for 2300 cycles. As an electrolyte we used H_2SO_4 0.3 M at 274 K. After this process the excess of aluminum was removed using $CuCl_2$/HCl solution. Finally, in order to obtain a membrane, the alumina layer was treated with H_3PO_4 water solution 5% (w/w) to open the pores. To synthesize 2D alumina templates, to compare the surface area, the procedure was the same that for the 3D templates, however the anodization was carried out using a constant voltage of 20 V.

2.3. Synthesis of 3-D PEDOT nanowires

A gold layer was deposited over one side of the 3-D alumina membrane trough thermal evaporation. The electrochemical synthesis of PEDOT was carried out at room temperature in a three electrode cell. The working electrode was a gold coated alumina membrane attached in a steal adapter. A platinum grid acted as the counter-electrode and the Ag/AgCl electrode acted as the reference one. PEDOT was polymerized from a 0.01 M solution of EDOT and $LiClO_4$ 0.1 M in acetonitrile.

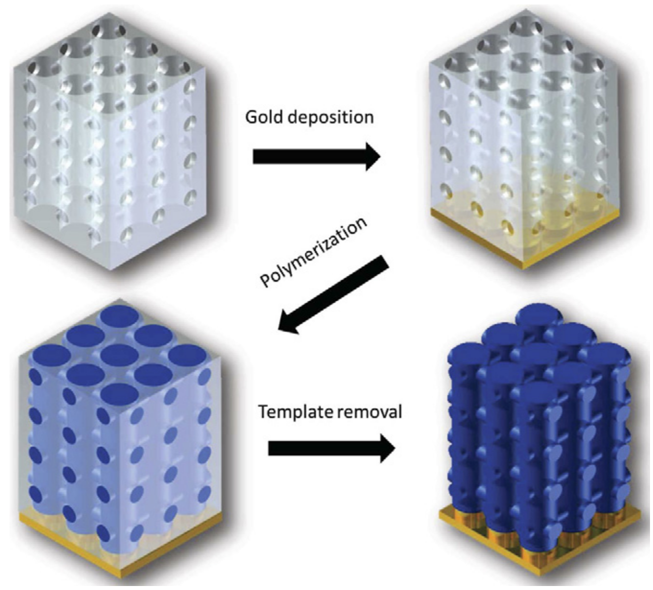

Fig. 1. Scheme of the synthesis of 3-D PEDOT nanowires.

The electrochemical polymerization was made at a deposition intensity of 3 mA during 4 h. The polymerization of PEDOT bulk was carried out using the same conditions ass that for 3-D PEDOT nanowires, however in this case the working electrode was a PET

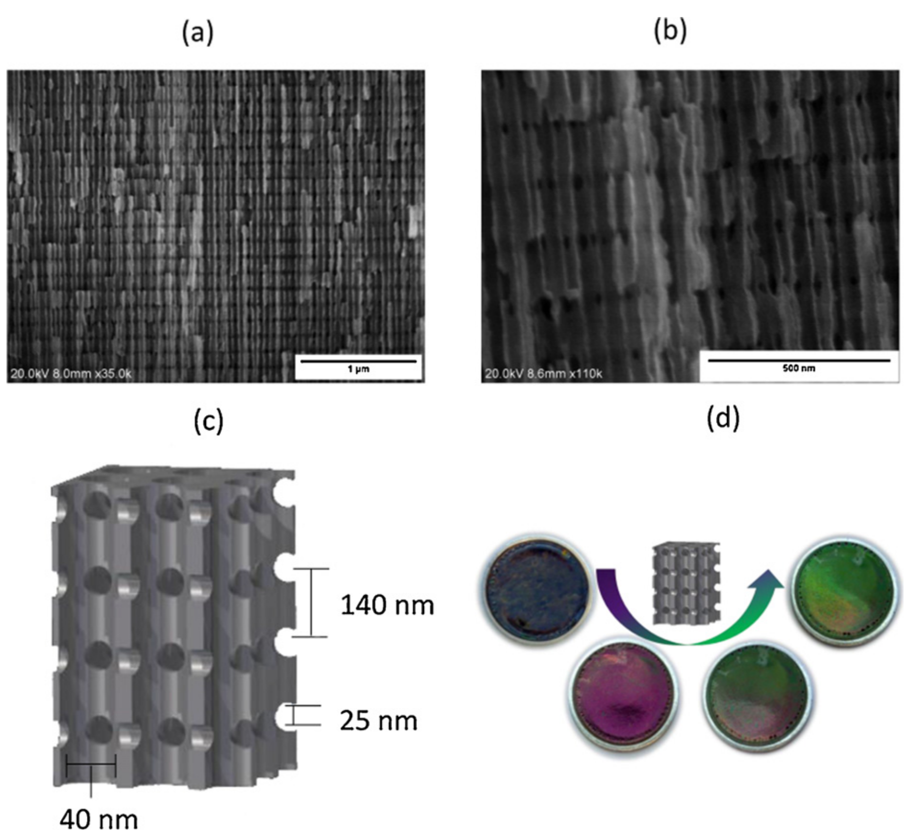

Fig. 2. (a) and (b) SEM images of the cross section of 3D alumina templates. (c) Characteristic distances between the different pores and (d) optical photographs of a 3D alumina templates taken from different viewing angles.