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Quasi-ordered P3HT nanopillar-nanocap structures with controlled size

A. Santos, P. Formentin, J. Pallarés, J. Ferré-Borrull, L.F. Marsal *

Departament d'Enginyeria Electrònica, Elèctrica i Automàtica, Universitat Rovira i Virgili, Avda. Països Catalans 26, 43007 Tarragona, Spain

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ABSTRACT

A fast and cost-effective technique is applied for fabricating an innovative nanostructure based on Poly(3-hexylthiophene). Such nanostructure consists of nanopillar arrays on a substrate of hexagonally quasi-ordered nanocap arrays of the same polymer. In this fabrication process, hybrid nanoporous anodic alumina fabricated by applying an asymmetric anodization process is used as template. The resulting nanostructure is replicated from the template via spin-coating and melt-assisted wetting methods. In addition, such nanostructure can be fabricated with a large quantity of structural configurations and materials. As a result of this versatility, it would be possible to use this nanostructure for fabricating a new kind of ordered bulk-heterojunction solar cells with enhanced efficiency.

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1. Introduction

An increasing attention has been paid to the development of nanometric-size structures such as nanotubes, nanowires and nanorods owing to their possible application in research fields like magnetic data storage [1], optoelectronics [2], sensors [3] and actuators [4]. Nowadays, it is possible to fabricate such polymeric nanostructures by nanolithography [5], mechanical patterning [6] and electro-spinning [7]. However, in order to produce highly-ordered polymeric nanostructures [8–10], the most vastly used method has become the template synthesis using nanoporous moulds. The main reason is that it is a cost-effective fabrication technique. So far, nanoporous anodic alumina templates (NAATs) have become a material widely used as pattern for their architectural features (pore density, pore diameter distribution, interpore distance and thickness). Through a two-step anodization process [11], we can fabricate NAATs with quasi-hexagonally arranged pores in an inexpensive way. Recently, a new type of nanostructures based on porous anodic alumina has been developed and studied from applying an asymmetric two-step anodization process [12,13]. These nanostructures, so-called hybrid nanoporous anodic alumina templates (HNAATs), are a promising material in order to be used for developing novel nanostructures and nanodevices. One interesting functionalization of HNAATs is the infiltration of their pores with polymers, which have many potential applications owing to their physical and chemical properties (transparency, pliability, biocompatibility, biodegradation, etc.). In that regard, among the thiophene family, Poly(3-hexylthiophene) (P3HT) is a suitable conjugated polymer for being used in polymer-based photovoltaic cells. The efficiency of these solar cells can be increased by means of nanostructured bulk-heterojunctions in which the interfacial distance between the donor and the acceptor phases is lower than 20 nm [14].

In this work, we present a method for fabricating nanopillar-nanocap structures based on P3HT by using HNAATs as pattern. The applied technique consists of a combination between the spin-coating and the melt-assisted template wetting methods. The resulting nanostructure consists of P3HT nanopillars on a substrate of P3HT quasi-hexagonally arranged nanocaps. The structural features are analyzed in detail through ESEM (environmental scanning electron microscope) images. This nanostructure could be integrated into a new kind of high-efficient polymer-nanostructured solar cells.

2. Experimental

2.1. Fabrication of hybrid nanoporous anodic alumina templates

High-purity (99.999%) aluminium (Al) sheets were pre-treated following the procedure reported elsewhere [12]. The hybrid nanoporous anodic alumina templates were fabricated using direct anodization of those aluminium substrates in an electrochemical cell following an asymmetric two-step anodization process. The first anodization step consists of applying the anodization voltage directly (170 V) in an electrolyte aqueous solution of phosphoric acid (H_3PO_4) (0.3 M). The resulting nanostructure is a thin film of nanoporous alumina with disordered pores (Fig. 1a). When the first anodization step finished, the aluminium oxide (Al_2O_3) film was dissolved by wet chemical etching using a mixture of phosphoric acid (H_3PO_4) (0.4 M) and chromic acid ($H_2Cr_2O_7$) (0.2 M) at 70 °C during the same time of

* Corresponding author.
E-mail address: lluis.marsal@urv.cat (L.F. Marsal).

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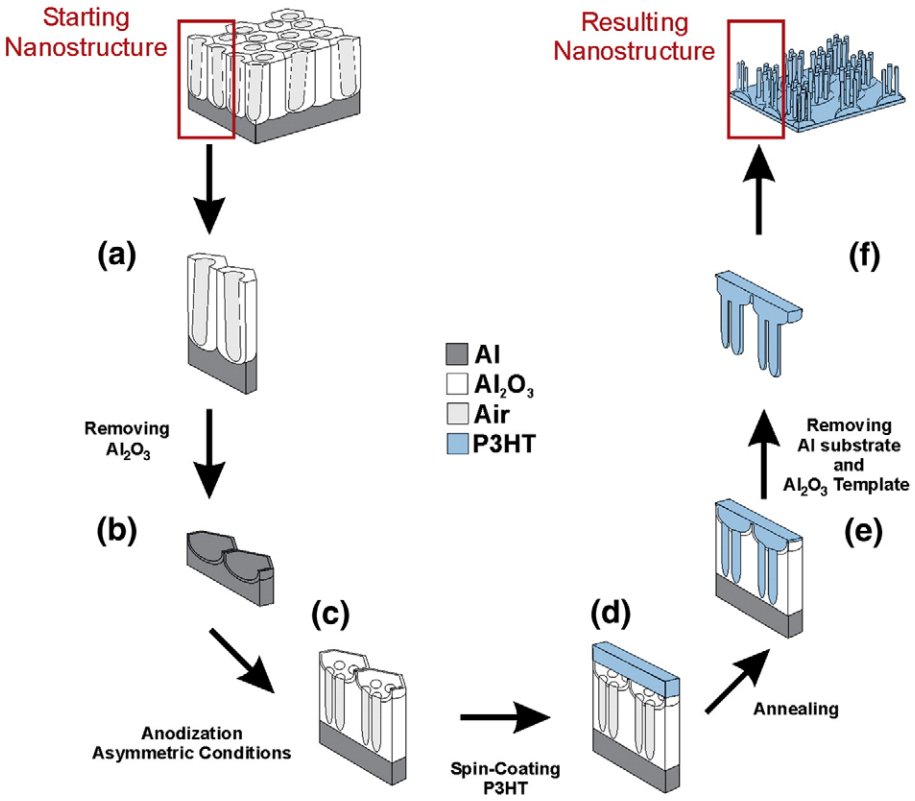

Fig. 1. Slanted cross-section view diagram describing the fabrication process of the P3HT nanostructure. (a) NAAT after the first anodization step (disordered pores). (b) Pre-patterned aluminium surface after removing the NAAT. (c) HNAAT after the second anodization step (subpores grow inside pores). (d) Spin-coated HNAAT with P3HT. (e) HNAAT infiltrated after annealing. (f) Substrate of P3HT nanocaps with nanopillars on their top.

the first anodization step (about 30 min). As result, a pre-pattern was produced on the aluminium surface (Fig. 1b). Afterwards, the second step of the anodization process was conducted under asymmetric anodization conditions (40 V) in an aqueous solution electrolyte of oxalic acid ($H_2C_2O_4$) (0.3 M). So, a HNAAT, which consists of an outward hexagonal lattice of large pores in whose interior smaller pores grow, was fabricated (Fig. 1c). The anodization voltage (40 V) was maintained for 3 min, when the hybrid nanoporous anodic alumina template reached a suitable thickness (about 500 nm). After anodization, a slight pore widening was carried out by wet chemical etching in 5 wt.% aqueous phosphoric acid at 35 °C for 10 min in order to facilitate the infiltration process of the pores.

2.2. Fabrication of the P3HT nanostructure

Once the anodization process was finished, the HNAATs were infiltrated with Poly(3-hexylthiophene). First, the samples were spin-coated (2000 rpm, 30 s) by a drop of a chloroform (CH_3Cl) solution of P3HT (10 wt.%) (P3HT, melting point 238 °C, M_w ~17500 g mol^{-1}, 99.995% regioregularity, Sigma-Aldrich) (Fig. 1d). Secondly, the covered hybrid nanoporous anodic alumina templates were annealed at 250 °C for 30 min in air for injecting the polymer into the pores by melt-assisted wetting (Fig. 1e). Finally, the samples were slowly cooled to room temperature and the remaining Al substrate was removed in a saturated mercuric chloride solution ($HgCl_2$). The HNAATs were dissolved in a solution of sodium hydroxide (NaOH) (1 M) at room temperature (Fig. 1f).

2.3. Characterization

The structural features of both the HNAATs and the replicating polymeric nanostructures were characterized by an environmental scanning electron microscope (ESEM FEI Quanta 600). In order to compare the geometric features of the templates with the corresponding features of the moulding nanostructures, we measured the interpore ($d_{interpore}$) and the intersubpore ($d_{intersubpore}$) distance (centre-to-centre pore and subpore distance, respectively), the pore (d_{pore}) and subpore ($d_{subpore}$) diameter, the intercap ($d_{intercap}$) distance (centre-to-centre cap), and the cap (d_{cap}) and pillar (d_{pillar}) diameter by ESEM images using a standard image processing package (ImageJ, public domain programme developed at the RSB of the NIH, USA). The results obtained are summarized in Table 1S (see Appendix A). A Gaussian fit was used to calculate the average of each structural feature ($d_{interpore}$, $d_{intersubpore}$, d_{pore}, $d_{subpore}$, $d_{intercap}$, d_{cap} and d_{pillar}) while the standard deviation was used as an estimation of the dispersion in the measurements (see Fig. 1S in Appendix A).

3. Results and discussion

3.1. Template image analysis

The current density (J) and voltage (V) versus time (t) characteristics corresponding to the fabrication process of the hybrid nanoporous anodic alumina templates are showed in Fig. 2. As previous works reported [12,13], the main difference between symmetric and asymmetric two-step anodization processes is that, during the second step of the asymmetric process, there is a shift in the minimum of J. This fact is due to the decrement of the anodization voltage with regards to the applied anodization voltage in the first step implies a reduction in the lattice constant. So, subpores (pores with smaller diameters) grow inside the hemispherical hollows (pores with large diameters) on the HNAAT surface (Fig. 3a and b). Before infiltration, the HNAATs were analyzed by ESEM image analysis. As we can see in Table 1S, the average interpore and intersubpore distances were 398 nm and 101 nm, respectively, and

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