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Wetting in nanopores of cylindrical anodic aluminum oxide templates: Production of gradient polymer nanorod arrays on large-area curved surfaces

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ABSTRACT

Although the fabrication of nanostructures has been investigated extensively, it is still a challenge to prepare nanostructures or nanostructure arrays on curved surfaces. In this work, we develop a simple and novel method to fabricate polymer nanorod arrays on large-area curved polymer surfaces with controlled curvatures. This method is based on the wetting of polymer melts in the nanopores of cylindrical anodic aluminum oxide templates, which are prepared by electrochemical anodization of aluminum wires. Polymers such as poly(methyl methacrylate) (PMMA) melts can wet the nanopores of the templates via capillary force after thermal annealing, resulting in the formation of PMMA nanorod arrays with gradient heights on curved PMMA surfaces. This work not only opens up new possibilities for creating non-planar surfaces with desired nanostructures, but also contributes to a deeper understanding of wetting behavior in confined geometries.

1. Introduction

In recent years, nanostructures have attracted great attention because of their unique properties and applications in solar cells, drug delivery, sensors, biomarkers, and catalysts [1–3]. Many fabrication methods have been developed to prepare nanostructures or nanostructure arrays, and these methods are usually applied to flat substrates [4]. Although nanostructures grown on flat substrates are sufficient for most applications, nanostructures on curved surfaces are required for certain practical applications such as lens and curved windows [5]. Therefore, it is of crucial importance to develop new and improved fabrication methods for making nanostructures or nanostructure arrays on curved surfaces, which offer more design and processing flexibility.

There have been relative few reports on the fabrication of nanostructures or nanostructure arrays on curved surfaces. For example, Sun et al. reported the preparation of nanostructured porous films on curved surfaces using a colloidal monolayer as a template [6]. In their work, colloidal monolayers with 1000 nm diameter PS spheres were first mixed with $SnCl_4$ precursor solutions. After the floating colloidal monolayer was picked up by a glass rod and calcinated at 500 °C, porous SnO_2 films were formed. Khan et al. also reported a nanopatterning method on curved surfaces [7]. A monolayer of SiO_2 spheres was first formed by self-assembly on a flat glass substrate. The monolayer of particles was then picked up by a flexible transparent sticky surface and placed on the curved substrate to be patterned. Finally, nanopatterns can be generated by irradiating the substrate with laser [7]. Recently, we also studied the fabrication of hierarchical polymer structures by wetting porous templates with electrospun polymer fibers [8]. Polymer nanorods were formed on the polymer fibers. The two size scales of ordering on the polymer structures

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can be controlled independently. The first length scale is controlled by the diameters of the electrospun fibers, and the second length scale is controlled by the pore sizes of the templates [8].

Although these methods can be used to fabricate nanostructures on curved surfaces successfully, it is still difficult to control the uniformity of the nanostructures. For example, the methods involving the transfer of microsphere monolayers onto curved surfaces suffer the problem of having different numbers of microsphere layers on the samples. Some regions on the samples may not be covered well by the microspheres, and defects are formed. In addition, nanostructures with high aspect ratios are usually difficult to form on curved surfaces.

To overcome these problems, here we develop a simple and versatile method for the fabrication of polymer nanorod arrays on large-area curved polymer surfaces. This method is a modified approach of the traditional template method using anodic aluminum oxide membranes. In the traditional template method, the anodic aluminum oxide membranes are formed by the anodization of flat aluminum sheets. The growth directions of the nanopores formed by the anodization process are perpendicular to the flat surfaces of the aluminum sheets. In this work, however, we fabricate curved templates by the anodization of cylindrical aluminum wires, in which the directions of the nanopores are perpendicular to the surface of the wire. After the curved templates are wetted by materials such as polymer melts, nanostructure arrays can be generated on curved surfaces. The advantage of using the curved templates is that the sizes and the aspect ratios of the nanostructures can be controlled by the nanopores of the templates, while the curvature of the curved surfaces can be changed using cylindrical wires with different radii.

In this study, we prepare the cylindrical anodic aluminum oxide (c-AAO) templates by the electrochemical oxidation of cylindrical aluminum wires with the wire diameter of ~500 μm. The diameters of the nanopores of the c-AAO templates are ~30 nm and can be further enlarged using phosphoric acid. The c-AAO templates are then wetted by poly(methyl methacrylate) (PMMA), and PMMA nanorod arrays with gradient heights can be generated on PMMA surfaces. The c-AAO templates possess curved geometries and can serve as unique templates for fabricating polymer, inorganic, or metal nanostructures on curved surfaces.

2. Experimental section

2.1. Materials

Poly(methyl methacrylate) (PMMA) (M_w: 97 kg mol^{-1}) was purchased from Sigma–Aldrich. *N*,*N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were obtained from Tedia. Isopropyl alcohol (IPA) was purchased from Mallinckrodt Chemicals. Ethanol was purchased from Echo. Perchloric acid was purchased from J. T. Baker. Oxalic acid and potassium dichromate were purchased from Alfa Aesar. Phosphoric acid and sodium hydroxide (NaOH) were purchased from Showa. Aluminum wires (diameter ~500 μm) were obtained from Alfa Aesar. Wipers (Kimwipes) were purchased from Kimberly-Clark.

2.2. Fabrication of the c-AAO templates

The c-AAO templates with ordered pores were made by the two-step anodization method, which was first developed by Masuda et al. and used previously for planar AAO templates [9]. At the beginning, a high-purity (99.9990%) aluminum wire was degreased in isopropyl alcohol (IPA) with sonication for 10 min. After the wire was cleaned by DI water, it was electropolished in ethanol/perchloric acid ($HClO_4$) (80:20) mixed solution by 20 V at 4 °C for 15 s. Subsequently, the aluminum wire was anodized at 40 V in 0.3 M oxalic acid ($H_2C_2O_4$) aqueous solution at 16 °C for 1 h. Next, the anodized aluminum wire was etched chemically in potassium dichromate ($K_2Cr_2O_7$) (1.8 wt%)/phosphoric acid (H_3PO_4) (6 wt%) solution to remove the aluminum oxide layer, leaving the pits behind. After that, the second anodization was performed under the same conditions as the first anodization except for longer times (2 h or more). The lengths of the nanopores are ~10 μm by the second anodization for 2 h. The diameters of the nanopores and the center-to-center distance of the c-AAO templates were ~30 and ~100 nm, respectively. The aluminum wire was then immersed in phosphoric acid (5 wt%) at 30 °C for 15 min to widen the pores. Finally, cylindrical anodic aluminum oxide (c-AAO) templates with an average pore diameter of ~40 nm were fabricated.

2.3. Fabrication of PMMA nanorod arrays on curved PMMA surfaces

At first, PMMA films were prepared by spin-coating or blade-coating. For example, a 10 wt% PMMA (M_w: 97 kg mol^{-1}) solution in THF was spin-coated on a glass substrate at 500 rpm for 10 s and 1000 rpm for 60 s. After the films were dried at room temperature, a cylindrical anodic aluminum oxide (c-AAO) template was placed on the top of the PMMA film. The sample was then covered by a glass substrate and fixed by a clip. Subsequently, the sample was annealed at 150 °C for 15 min. The c-AAO template was then dissolved by 5 wt% $NaOH_{(aq)}$. Finally, the sample was washed with DI water and dried at room temperature.

2.4. Structure analysis and characterization

The glass transition temperatures (T_g) of the polymers were measured by the differential scanning calorimetry (DSC) using a SEIKO Instruments EXSTAR 6000 DSC. The c-AAO templates and the polymer nanostructures were characterized by a JEOL JSM-7401F scanning electron microscope (SEM) at an acceleration voltage of 5 kV. The samples were coated with 4 nm of platinum before the SEM measurements.

3. Results and discussion

The traditional template method is commonly used to prepare one-dimensional nanostructures using porous