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Facile Preparation of Carbon Nanopillar Array

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Abstract: Carbon-based nanostructures have attracted extensive interest in obtaining advanced sensing electronic devices in environmental and biological monitoring applications as an alternative to conventional materials. Herein, the facile preparation, control of the growth, and artificial intelligence–based morphological information of the carbon nanopillar array in the Anodized Aluminum Oxide (AAO) template were investigated. A facile approach for controlling the growth of the nanostructure was proposed as a two-step anodization technique for AAO and Plasma Enhanced Chemical Vapor Deposition (PECVD) for carbon nanopillar array. It involved the competitive carbon deposition between the carbon nanopillars electrodeposited on the AAO template and at the bottom of the pores of AAO under vacuum conditions. The morphology and structure of the prepared carbon nanopillars were reported in detail. Hexagonally straight AAO nanotubes were approximately 65 nm in diameter and 360 nm in length, with 90 nm interpore distances. The AAO nanotube density is approximately 1.75×10^{14} cm^{-2}. Carbon nanopillars with a width of ~60 nm were used to create a low-dimensional nanostructure. This controllable preparation leads to the facile and impressive preparation of a free-standing carbon nanopillar array, especially for various chemical sensor applications.

Keywords: Carbon; nanopillar array; low-dimensional nanostructure; alumina; nanotube.

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INTRODUCTION

As nanomaterials offer unique mechanical, electrical, optical, and magnetic properties, they are drawing a tremendous amount of attention for many potential applications in nanodevices such as energy storage devices (batteries, supercapacitors, etc.), chemical sensors, and biological sensors (1–4). Nanomaterials are expected to play a key role in the devices by providing surface effects, small-size effects, and even quantum effects. Recent developments and current published research findings in the controlled growth of metal oxide nanowires have raised the need for the fabrication process of emerging high-performance and high-density nanoelectronic devices. A considerable amount of literature has been published on the fabrication of nanomaterials using different physical and chemical methods. More recently, the template-assisted method has been proposed to obtain next-generation functional nanomaterials with directional alignment and uniform size. In this sense, carbon nanostructures (nanotubes, nanopillars, nanofibers, etc.) attract attention as they have versatile redox-dependent properties and wide applications in catalysis, photochromism, electrochromism, energy storage, and chemical/bio detection (5–9).

There are several methods available for the preparation of carbon nanostructures (10–14) but up to date, only a few reports have been encountered describing the preparation of carbon nanopillars. Plasma processing techniques were used in the preparation of carbon nanomaterials. Wang *et al.*(15) prepared diamond nanocones by direct current plasma etching onto the diamond substrate in a methane/hydrogen atmosphere. Kunuku *et al.* (16) developed carbon nanocones and nanopillars using the reactive ion etching technique to modify the diamond surface. Zou *et al.* (17) fabricated carbon nanopillar arrays by modifying the nanocrystalline diamond film surface with the same technique. Ren *et al.* (18) prepared carbon nanostructures by controlling ion flux and energy in an inductively coupled plasma enhanced chemical vapor deposition (PECVD) system. On the other hand, it has been suggested to use the Anodic Aluminum Oxide (AAO) template assisted technique as a more useful technique in the preparation of carbon nanopillars (19–24). In 2017, Liu *et al*. prepared a novel template-based catalyst (Ni/anodic anodic AAO) to control the growth of carbon nanotubes with a uniform particle size distribution (25).

Recently, researchers have shown an increased interest in the fabrication of carbon nanopillar arrays. In previous studies, carbon nanopillar arrays were prepared by ion beam irradiation into AAO template. Despite its fabrication leading to success, the preparation of carbon nanopillars has a number of problems, such as high production costs and a complex mass production process in use. Taking into account the previous studies, this study investigated the preparation of carbon nanopillars using a dual-role of physical vapor deposition (PVD) technique and an AAO template assisted technique for a simple and low-cost preparation without coating with plasma or ion beam radiation. In this study, the proposed design method with a two-step anodization approach was used and optimized experimental conditions (temperature, time, and pressure) for the preparation of the novel nano-sized carbon nanopillar array. The motivation of this study is to develop a novel carbon nanopillar array in the AAO template to overcome the limitations of the conventional process with low temperature and vacuum. Furthermore, the AI–aided SEM imaging–based characterization of the carbon nanopillar array in the AAO template was investigated to determine the morphology.

EXPERIMENTAL SECTION

In previous methods, there have been some serious disadvantages, such as high-temperature annealing (150 °C–900 °C), high deposition pressure (10^{-5}-10^{-4} Torr), time-consuming nature (2–12 h), and the use of expensive instrumentation and chemicals (8,24,26). However, in this study, we have used a simple two-step anodization technique to obtain the carbon nanopillar array (temperature (60 °C), deposition pressure (10^{-6} Torr), and time (2 h). This study discussed the fabrication of the carbon nanopillar array. Furthermore, the novelty of this study was the fabrication and AI-assisted characterization of the structure of the carbon nanopillar array.

In this study, experimental stages consisted of four steps. In the first step, high purity titanium and then high purity aluminum (≥ 99.999%) were evaporated in a high vacuum environment on the Si wafer. In the second step, the Al film is anodized in a 0.3 M oxalic acid ($H_2C_2O_4$) solution at a constant applied voltage of 40 V in an environment of constant temperature of 5.0 ℃ for 10 min. Grown nanoporous AAO film was carried out to obtain AAO nanotubes by the wet etching process in a mixture of 6% (w/w) orthophosphoric acid (H_3PO_4) and 2% (w/w) dichromic acid ($H_2Cr_2O_7$) solution at 60 °C for 5 min. In the third step, prepared AAO films were anodized to obtain the AAO template under the same experimental conditions for 2 h and chemically etched away for 5 min in the second anodization. Finally, the carbon nanopillar array was prepared via PECVD of carbon on the AAO template under vacuum. The morphology of the prepared AAO template and carbon nanopillars were studied by Scanning Electron Microscopy (SEM) and Electron Diffraction Spectroscopy (EDS) (SEM, FEI QUANTA 450 model).

RESULTS AND DISCUSSION

The morphologies of the prepared AAO template and carbon coated AAO template were studied by SEM. Moreover, the chemical composition of the AAO template was studied by EDS. As shown in Figure 1, hexagonally straight AAO nanotubes prepared were approximately 65 nm in diameter and 360 nm in length, with 90 nm interpore distances. The AAO nanotube density was approximately 1.75×10^{14} cm^{-2}. The experimental results showed that it could be based on the electrodeposition on the AAO nanoporous template with controlled pore size and to integrate the nano-sized components due to the electrochemical system under vacuum conditions (27).

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The prepared carbon-coated alumina template was characterized to determine the surface property of the nanostructure by the SEM technique, which is one of the most used techniques (28) to determine surface topography and three-dimensional (3D) surface topography of nanostructures. Figure 2 shows the SEM images, Artificial Intelligence (AI) analysis, and EDS analysis of the carbon coated AAO template. As shown in Figure 2a-b, prepared vertically free-standing carbon nanopillars are roughly parallel to each other and vertically aligned to form an array with a high surface area as aimed. This can be explained by the higher packing density of nanostructures fabricated by AAO template-assisted preparation. Furthermore, the AI approach was used to obtain high-quality SEM micrographs of structures. The SEM image (8-bit/mpl-viridis mode) of the prepared carbon nanopillars was improved using the ImageJ software. In Figure 2c-e, AI-assisted SEM image (8-bit), SEM image (8-bit/mpl-viridis), 3D surface topography, and color histogram of the prepared carbon nanopillars were provided. The AI-assisted SEM image (8-bit/mpl-viridis) of the prepared carbon nanopillars was able to improve the SEM image quality of structures and to eliminate background noise in noisy low-contrast SEM images. Furthermore, the 3D topography of the prepared carbon nanopillars was able to enhance the surface characteristics of SEM images. The color histogram of the prepared carbon nanopillars was a representation of the distribution of colors in the SEM image (8-bit/mpl-viridis) of the prepared nanostructure. The AI-assisted method was used to offer not only low feature dimension but also detectable the surface property of the nanostructure, implying that it could detect the distribution in the structure in an effective manner. For the digital SEM image of the nanostructure, the color histogram was used to determine the basic red- blue- green channel (RGB) algorithm of the SEM image. The mean color value of the image was calculated using the distance values according to the minimum and maximum distance values. We compared the color histogram-based mean color values of the AI-assisted SEM image (8-bit/mpl-viridis) of the carbon coated AAO surface and prepared carbon nanopillars. Consequently, the obtained samples were highly uniform, nano-sized, and wire-shaped. Carbon nanopillars were obtained at approximately 60 nm (width). According to the EDS spectra from the nanopillar surface, the strong characteristic absorption peak of C was observed (Figure 2f). These EDS values were consistent with previous studies for carbon nanostructures (28,29).

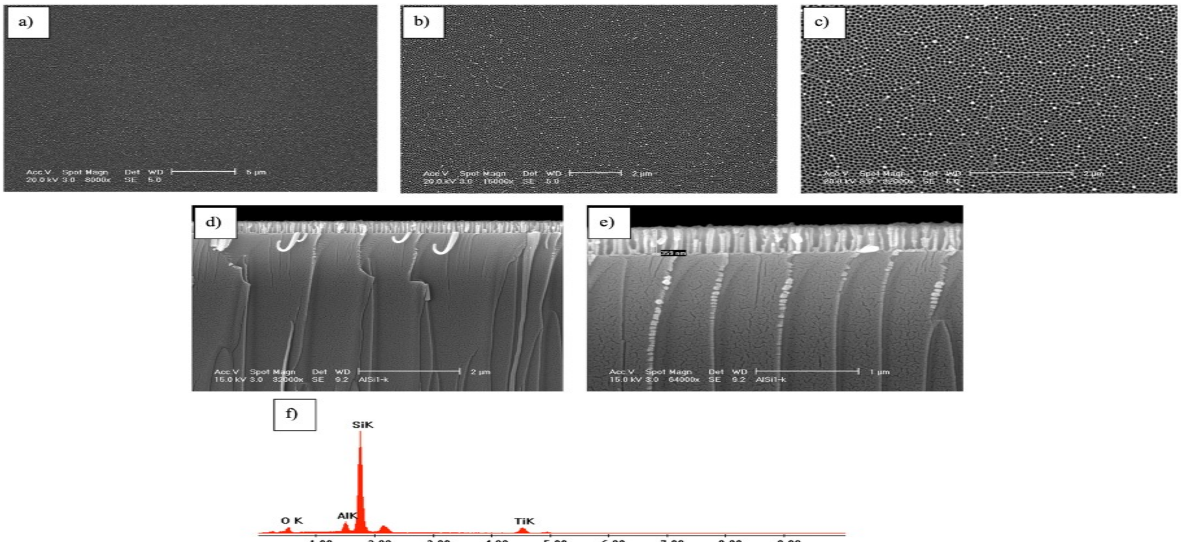

Figure 1: **(a-b-c)** SEM images from the surface (with different magnifications), **(d-e)** SEM images from the cross-section (with different magnifications), **(f)** EDS analysis of the prepared AAO template on Si.

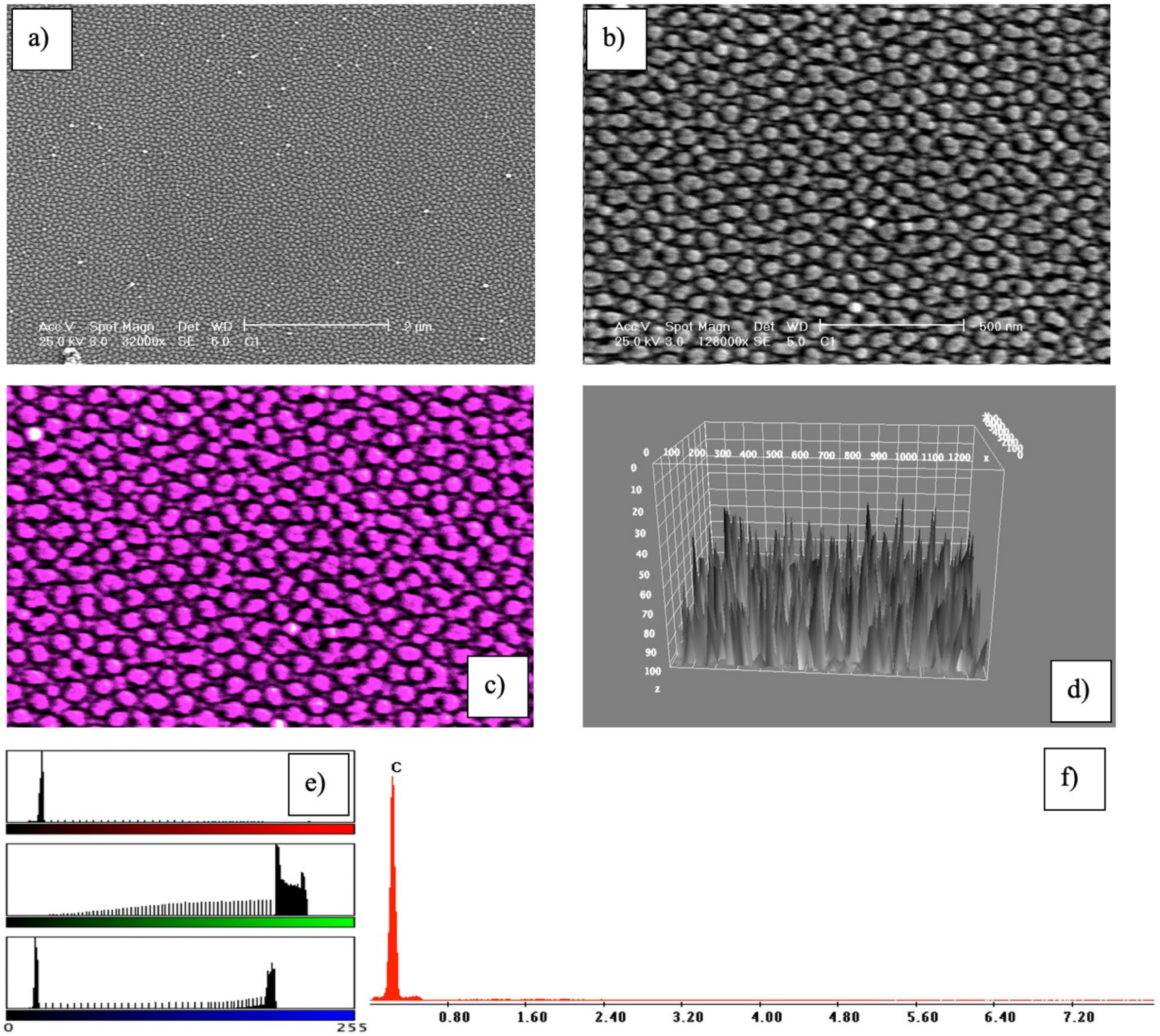

Figure 2: (a) SEM images at 32.000x, **(b)** SEM images at 128.000x, **(c)** SEM image (8-bit/magenta), **(d)** 3D surface topography, **(e)** color histogram, and **(f)** EDS analysis of the carbon nanopillars.

In this study, AAO template-assisted preparation of carbon nanopillars provided some remarkable advantages over the other methods. The carbon nanopillar array was prepared under mild conditions rather than requiring high temperatures, high vacuum, or expensive instrumentation. The carbon nanopillar array was prepared with controllable morphology due to the shape of the nanopores of the AAO template. The width of the carbon nanopillar can be tuned via the nanopore size of the AAO template in future studies. The results reveal that AAO template assisted preparation of carbon nanopillar array is one of the most prominent method.

CONCLUSION

The carbon nanopillar array was prepared by the AAO template-assisted technique. Hexagonally straight AAO nanotubes were approximately 65 nm in diameter and 360 nm in length, with 90 nm interpore distances. The AAO nanotube density is approximately 1.75×10^{14} cm^{-2}. Carbon nanopillars were obtained at approximately 60 nm (width). This controllable preparation leads to the facile and impressive preparation of free standing carbon nanopillar array, especially for various chemical sensor applications.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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AVAILABILITY OF DATA

The authors confirm that the data supporting the findings of this study are available within the article. Raw data that support the findings of this study are available from the corresponding author, upon reasonable request.

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