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Novel Fabrication of Ag Nanostructures by Template-Based and Photo Reduction Method

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Abstract

In this work, fabrication of silver nanostructures with different morphologies has been grown on anodic aluminum oxide templates that anodized in three different acid electrolytes. Photo-reduction method used to deposit these nanostructures under novel UV irradiation (366 nm) technique. FESEM results prove formation of Ag nanostructures depending on shape of and diameter of pores. This simple and environmentally safe method open new fields to use Ag structures with controllable and nanosize dimensions in several applications.

Keywords: anodic aluminum oxide, photoreduction method, Ag nanostructures.

الخلاصة

في هذا العمل, تم تحضير الفضة بتراكيب نانوية وبأشكال مختلفة بواسطة انمائها على قوالب اوكسيد الالمنيوم المأنود بواسطة ثلاثة حوامض الكتروليتية مختلفة. تم استخدام طريقة الأختزال الضوئي لأجراء عملية الترسيب وبتسليط الأشعة فوق البنفسجية التي تعتبر نادرة الأستخدام في تحضير الفضة بهذه الطريقة (وبطول موجي 366 نانومتر). لقد اضهرت نتائج فحوصات المجهر الماسح الضوئي تشكّل الفضة بتراكيب نانوية مختلفة معتمدتاً على شكل وحجم ثقوب القالب المستخدم. ان هذه الطريقة البسيطة والامنة بيئيا تفتح مجالات جديدة لاستخدام تراكيب الفضة المسيطر على ابعادها النانوية واشكالها في تطبيقات عدة.

Introduction

Recently, template synthesis of useful nano-materials has attracted significant considera-tion. This is mainly owing to possibility to con-trol diameter, length, and density of manufac-tured nanostructures by varying template and/or deposition factors. In particular, porous anodic aluminum oxide (AAO) has grown into a common template for production of, e.g., nanotubes (NTs) and nanowires (NWs) of met-als and ceramics. AAO is thermally stable and contains straight and orderly nanochannels at a high density (109–1011 per cm^2) [1][2]. Scien-tific attention has been focused not only on production of various nanostructured materials, but also on their technological and industrial uses [3]. Metallic silver, as a multifunctional material, and its nanostructures have concerned a lot of benefits. Its nanostructures have been widely brought together in pores of porous AAO templates by a variety of methods [4][5][6].

In this paper, we develop a novel process for making crystalline Ag *via* photoreduction method supported by AAO templates. During this process, UV irradiation aids to reduce $AgNO_3$ and produce Ag nanostructures inside channels of AAO templates.

Materials and Methodology

Anodization was achieved using three different acidic aqueous solutions, based on oxalic, tar-taric and phosphoric acids correspondingly. In case of oxalic acid, anodization was performed at a constant voltage of 40 V, while in case of tartaric and phosphoric acids at a constant volt-age of 195 V. Values of voltages used were in range of optimum values, supportive to litera-ture [7][8][9].

Aluminum foil was purchased from Alfa Asser with 99.99% purity and thickness of 150 µm was cut into 2.5 cm^2 × 2.5 cm^2. Specimens were polished mechanically to 1200, 2000 using SiC waterproof paper, washed with acetone and distilled water, by sonication technique for 10 min in each stage. Specimens were annealed at 550 ºC inside a furnace (in air) to remove stress from sample surface and increase grain size of Al specimens [10]. After furnace was cooled to room temperature, specimens were dipped in 5 wt% NaOH solution to eliminate native oxides spreading to surface of Al specimens. A handmade Teflon cell was used to start electrochemical polish, in which aluminum foil was pushed against a Cu plate that connected to a positive electrode of power supply and a platinum foil coupled to negative electrode was used as counter. Electropolish bath of perchloric acid: ethanol 1:10(v/v) with 14 V (DC) was applied for 7 min at a constant temperature and magnetic stirring to dispense generated heat [11].

AAO templates were generated by anodizing polished Al by a two-step anodization like to electropolishing. Electrochemical anodization was done in different acid solutions. To anodize aluminum foil, 0.3 M oxalic acid was used and two anodization steps were applied; anodization was extended to 7 h in each step with 40 V (DC), constant chemical cell temperature at 5 ºC, and magnetic stirring.

Aluminum oxide that formed after first anodization step was detached by immersing foil in a mix of 6 wt% phosphoric acid (Pi 85%) and chromic acid solution with temperature variety from 60 ºC to 70 ºC for 55 min to get ordered pore arrays [12]. For anodization in phosphoric acid, two-step anodization was completed at 0.1 M with 195 V (DC) with a constant temperature at 5 °C, and anodization time was extended to 1.5 h in each step. Anodization in 0.3 M tartaric acid ($C_4O_6H_6$) was done with an applied anodizing voltage of 195 V (DC) at 5 °C for 70 min for each anodization step. Specimens were immersed in 5 wt% H_3PO_4 for 30 min to increase pore diameter, then washed thoroughly in distal water.

Fabrication of Ag nanostructures was achieved via photoreduction deposition method, in which 0.25 mmol of $AgNO_3$ was dissolved in deionized water by stirring for 10 min. Then, AAO template was immersed in solution and sonicated for approximately 180 s to enhance penetration of solution into pores. Subsequently, sample with solution was put under 366 nm UV irradiation (CAMAG Company) for 1 h to fabricate Ag nanostructures. AAO templates were picked up from solution and rinsed with distal water to remove residual materials.

As-grown Ag NSs morphology and surface properties onto AAO templates were characterized by field emission electron microscope (FESEM, Hitachi-54160, Japan). Crystalline of structures and phase establishment of prepared Ag with different aging time were determined by X-Ray diffraction analysis (XRD-600, Shimadzu, Japan) with Cu-Kα radiation (λ=0.1540 nm) at an applied voltage of 40 KV and (2Θ) with scan range from 10^o to 80^o.

Results and Discussion

Figure 1 shows the images of the AAO template prepared in phosphoric acid electrolyte it is noted that pores growth in AAO template are uniform and ordered regularly.

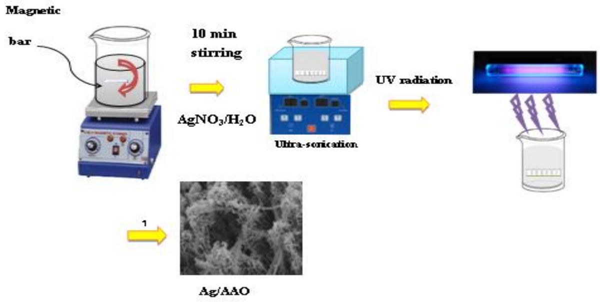

Figure 1: Graphical arrangement synthesis of Ag nanostructures (NSs) in AAO templates pores by photoreduction method.

Pore diameters of template prepared via oxalic, tartaric and phosphoric acids are about 44nm, 70nm, and 165 nm respectively that were calculated by image J program. AAO templates with this large pore diameter are used as support to growth Ag NSs by using photoreduction method.

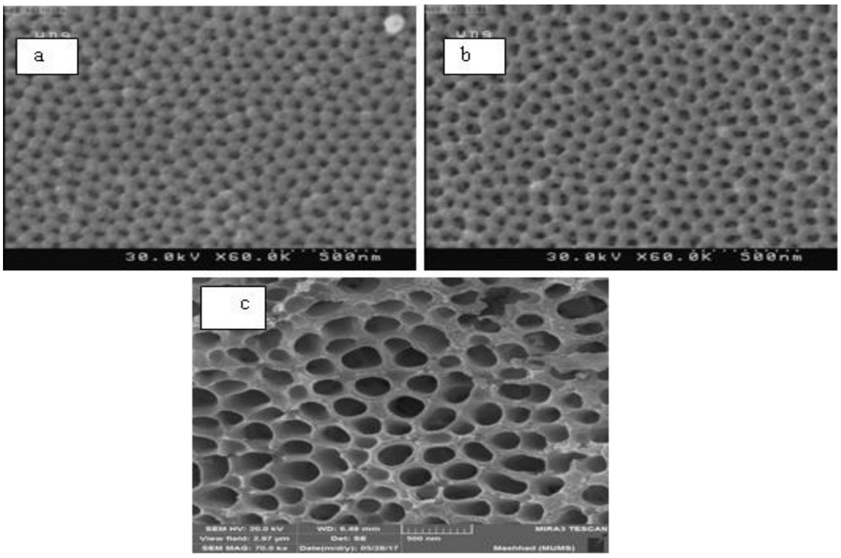

Figure 2: FESEM images top view of (a) AAO template. Anodization was directed in 0.3M $H_2C_2O_4$ under 40 V at 5 $^{\circ}C$. (C) AAO template in 0.3M ((CHOHCOOH) $_2$) under 195 V at 5$^{\circ}C$. (e) AAO template in 0.1 M H_3PO_4 at 5$^{\circ}C$.

As UV light irradiated upon AAO template, only a small ratio of its energy was scattered away or reflected back from template surface; most of incident energy was entered into and absorbed by template pores and solidified silver nitrate in the pores. If UV intensity was high, absorbed energy could be collected rapidly, which resulted in a rapid increase in template temperature and caused decomposition of $AgNO_3$. Silver particles were precipitated through step of [13][14].

$$2AgNO_3 \rightarrow 2Ag + 2NO_3 \uparrow + O_2 \uparrow \ldots\ldots\ldots(1)$$

A complete Ag growing process can be separated into two main stages: particle precipitation stage and particle growth and fusion stage. At first stage, precipitated particles were initially small and scattered in pores. Both particle size and number density were monotonically decreased along light propagating direction because UV intensity decayed exponentially with its propagation.

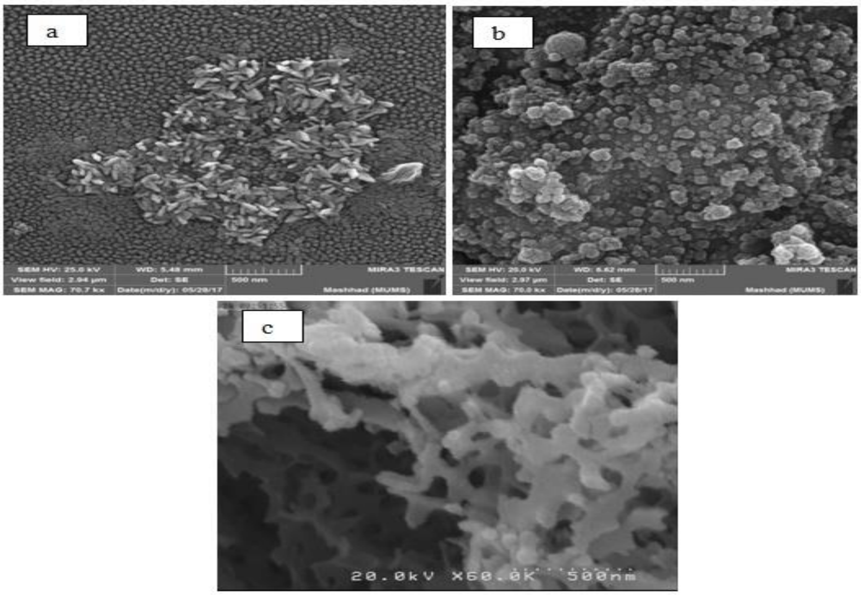

Figure 3:. Top view images of Ag nanostructures grown on AAO template anodized in (a) oxalic acid (b) tartaric acid and (c) phosphoric acid by photoreduction method.

This study, which consider firs global research appears different nanostructure shapes onto AAO templates from a cluster of reefs among nanorod arrays to Ag nanoparticles and nanonecklaces like structures.

The XRD spectrum of Ag (NSs) prepared by photoreduction on AAO template is shown in Figure 4. The peak is centered at 2Θ 38.240 and assigned to (111), which are identical with that of the Ag material. This method provided satisfactory NPs distribution along the AAO template surfaces and good crystalline structure of Ag nanomaterials.

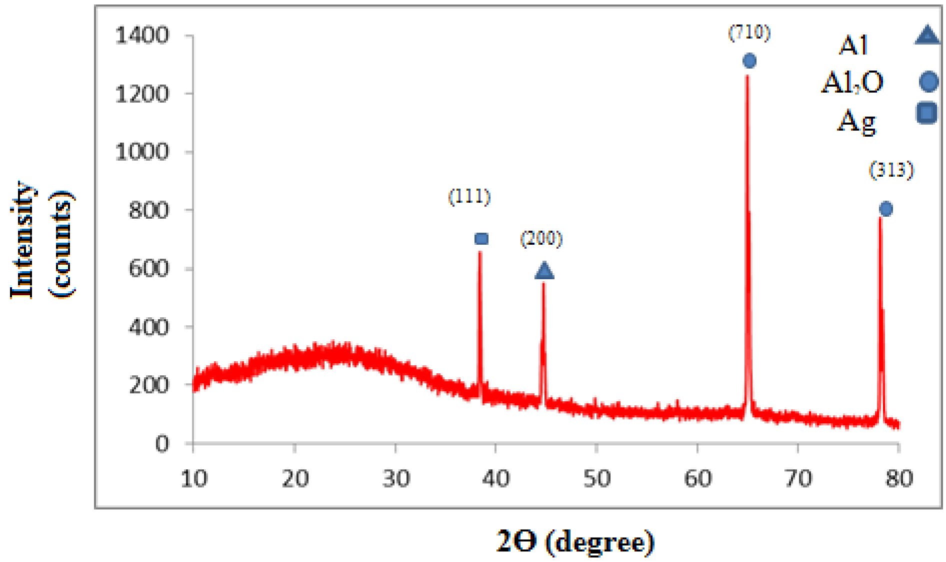

Figure 4: XRD pattern of Ag (NSs) as- grown by photo reduction method on AAO templates.

Conclusions

Anodic aluminum oxide templates (AAO) were synthesized in three different electrolyte acids with tow step anodization. Ag nanostructures at various morphologies grown on AAO templates by photoreduction method. This simple and safe environmental method appears high capability to produce silver nanostructures at high surface area with high ordered distribution, lead to open new filed to optoelectronic and surface applications, especially, surface Plasmon and antibacterial technologies.

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