Applied Surface Science xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Large-area and cost-effective fabrication of Ag-coated polymeric nanopillar array for surface-enhanced Raman spectroscopy

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ARTICLE INFO

Article history:
Received 13 October 2017
Revised 5 February 2018
Accepted 8 February 2018
Available online xxxx

Keywords:
Surface-enhanced Raman scattering
Silver nanoparticle
Nanopillar array
Anodic aluminum oxide
Reproducibility

ABSTRACT

The throughput and cost of surface-enhanced Raman scattering (SERS) substrates are considered the main obstacles for widespread commercialization of this spectroscopy technology. Here, we demonstrate a facile, large-area, and cost-effective method for fabricating SERS substrates based on Ag-coated polyurethane acrylate (PUA) nanopillar arrays. Using a multistep anodization-widening and replication process we could cost-effectively produce the shape-controlled nanopillars and observed a unique beer-bottle morphology arranged in large-area of ca. 150 mm × 95 mm. Due to the softness and flexibility of PUA, the porous anodic aluminum oxide (AAO) template was repeatedly reused without requiring etching of the template to improve the reproducibility of nanopillar arrays. When the beer-bottle-shaped nanopillar array was uniformly coated with Ag nanoparticles and then thermally aged at 50 °C, the resulting SERS substrate exhibited a high enhancement factor of 2.8×10^6 with a low relative standard deviation of 9.0%. The linear sensitivity of our SERS substrate was also demonstrated, indicating that such a method is promising for developing Ag-coated nanopillar arrays suitable for quantitative chemical sensing.

1. Introduction

Surface-enhanced Raman scattering (SERS) spectroscopy is one of the most versatile tools for real-time detection of trace amounts of chemicals and can provide specific structural and vibrational fingerprints of the analytes of interest [1,2]. Since the first report of the technology by Albert and Creighton [2], SERS spectroscopy has been recognized as a crucial strategy for overcoming the main drawback of standard Raman spectroscopy, i.e. a low signal-to-noise ratio where only one out of 10^8 photons undergoes Raman scattering [3,4]. When molecules are close to a novel metal surface, the intensity of Raman scattering can be dramatically enhanced owing to long-range electromagnetic effect and a short-range chemical effect [5,6]. The electromagnetic field is highly localized and magnified in spatially narrow regions, typically referred to as ‘hot spots’, through excitation of localized surface plasmon resonances [7,8]. Therefore, significant efforts have been made to fabricate various noble metal nanostructures to improve the quality and number of ‘hot spots’ that are gaps between two adjacent noble metal structures, such as nanoscopically sharp tips, interparticle gaps, and nanopores [1]. However, many challenges remain in the fabrication of highly reproducible SERS substrates with low SERS signal variations [9]. Since these hot spots are usually scarce, it is practically impossible to obtain both high sensitivity and good signal reproducibility over a large area [10]. Therefore, enhancing the uniformity of ‘hot’ SERS-active nanostructures is crucial to ensure a narrow distribution of high enhancement factor values and high reproducibility.

In order to address this challenge, the fabrication of uniform SERS-active nanostructures has been demonstrated using various nanofabrication methods, such as photolithography, e-beam lithography, femtosecond laser ablation, and reactive ion etching (RIE) [11–13]. Ordered nanowire arrays fabricated using lithography or RIE techniques have shown low relative standard deviation (RSD) values around 25% with high enhancement factors [14,15]. In spite of the high enhancement of the SERS signal, conventional nanofabrication processes have still high cost and low throughput and hence their widespread commercialization is limited. Therefore, an inexpensive and easy fabrication method is required for the successful commercialization of highly sensitive and reproducible SERS substrates.

Recent works have demonstrated the use of anodic aluminum oxide (AAO) templates in the large-area fabrication of highly ordered nanoporous structures. For example, gold and silver were

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https://doi.org/10.1016/j.apsusc.2018.02.088
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Please cite this article in press as: A.N. Kim et al., Large-area and cost-effective fabrication of Ag-coated polymeric nanopillar array for surface-enhanced Raman spectroscopy, Appl. Surf. Sci. (2018), https://doi.org/10.1016/j.apsusc.2018.02.088

deposited in the pores of AAO templates and then the aluminum oxide layer was sacrificially removed, yielding size-selected metal nanopillar arrays for use as highly sensitive SERS substrates [2,16]. However, in this case, the efficiency and reproducibility of this technique is seriously low as the AAO needs to be etched to expose the nanopillar array.

Herein, we report a facile, large-area and cost-effective method for fabricating polyurethane acrylate (PUA) nanopillar arrays with different shapes for use as SERS substrates using a multistep anodization-widening and replication process. This method enabled us to cost-effectively produce the shape-controlled nanopillar arrays in large area owing to the utilization of commercially available anodization process. And, the AAO template could be repeatedly reused, improving the reproducibility of nanopillar arrays and sustainability of the process, since the nanopillar arrays were fabricated with soft and flexible PUA without requiring etching of the template. The PUA nanopillar arrays were decorated with SERS-active Ag nanoparticles and their sensitivity and reproducibility as SERS substrates for the detection of rhodamine 6G was investigated.

2. Materials and methods

2.1. Anodization of aluminum

High-purity aluminum sheet (99.999%) with a thickness of 0.5 mm was used for anodization experiments. Large-area aluminum sheets (150 mm × 95 mm) were cleaned in an ultrasonic bath with acetone for 5 min, rinsed in an ethanol bath, and then dried in a vacuum oven at 25 °C. Then, the aluminum sheet was electropolished in a mixture of perchloric acid and ethanol (3:7, v/v) under a constant voltage of 20 V at 0 °C for 210 s to remove the air-oxidized layer. This procedure resulted in a flat, smooth aluminum sheet with a shiny surface. A two-stage anodization method was used to prepare the AAO templates. In the first stage, anodization was conducted in an aqueous solution of 0.3 M oxalic acid under 40 V at 0 °C for 5 h. Then, the anodized aluminum oxide layer was etched away by dipping the sheet in a mixture of 1.8 wt.% chromic acid and 6 wt.% phosphoric acid at 60 °C for 24 h. To obtain an AAO template with a pore depth of 180 nm, a second anodization was carried out at 40 V at 0 °C for 264 s. Then, the pores were widened to 80 nm by immersing the AAO in a 0.3 M oxalic acid solution at 40 °C for 146 min. For controlling the shape of the pores, the duration of the second anodization and pore-widening process was divided, as shown in Fig. 1.

2.2. Fabrication of polymer nanopillar array

The AAOs were used as master templates for the replication of nanopillar arrays. UV-curable PUA resin (311RM, Minuta Tech) was dropped on the AAO template and a PET film was gently placed onto the resin layer as a substrate. Before PET deposition, the AAO was immersed in a 2 mM 1H, 1H, 2H, 2H-heptadecafluorodecyl phosphonic acid solution at 50 °C to facilitate removal of the polymer from the AAO. The PUA layer on the AAO was pre-irradiated with UV light ($\lambda = 365$ nm) for 140 s and was manually peeled off the template. Finally, the samples were further exposed to UV light for 24 h to ensure complete curing of the PUA film.

2.3. Synthesis of Ag nanoparticles

In a typical synthesis of Ag nanoparticles, 0.849 g of silver nitrate ($AgNO_3$) and 0.05 ml of oleic acid were mixed in a three-neck round-bottom flask containing 100 ml of oleylamine with mild stirring at 60 °C. Then, the reaction mixture was heated at 180 °C for 1 h under a nitrogen atmosphere until the color of the solution changed to dark brown. After cooling the resulting solution to 25 °C, an excess of acetone was added to the mixture, following by centrifugation for 8 min at 8500 rpm and then redispersion in 50 ml of hexane. The above process was repeated to remove the excessive oleylamine and byproducts. Finally, the precipitate was dissolved in cyclohexane and freeze-dried with liquid nitrogen.

2.4. Coating of Ag nanoparticle on PUA nanopillar array

The freeze-dried Ag nanoparticles were dispersed in toluene with a concentration of 2 wt.%. Ag-coated SERS substrates were prepared by dipping the as-prepared PUA nanopillar array film in the nanoparticle solution and withdrawing it at a constant rate with an angle normal to the solution surface at ambient temperature. Then, the substrate was vacuum dried to completely remove the solvent and aged at various temperatures for 1 h.

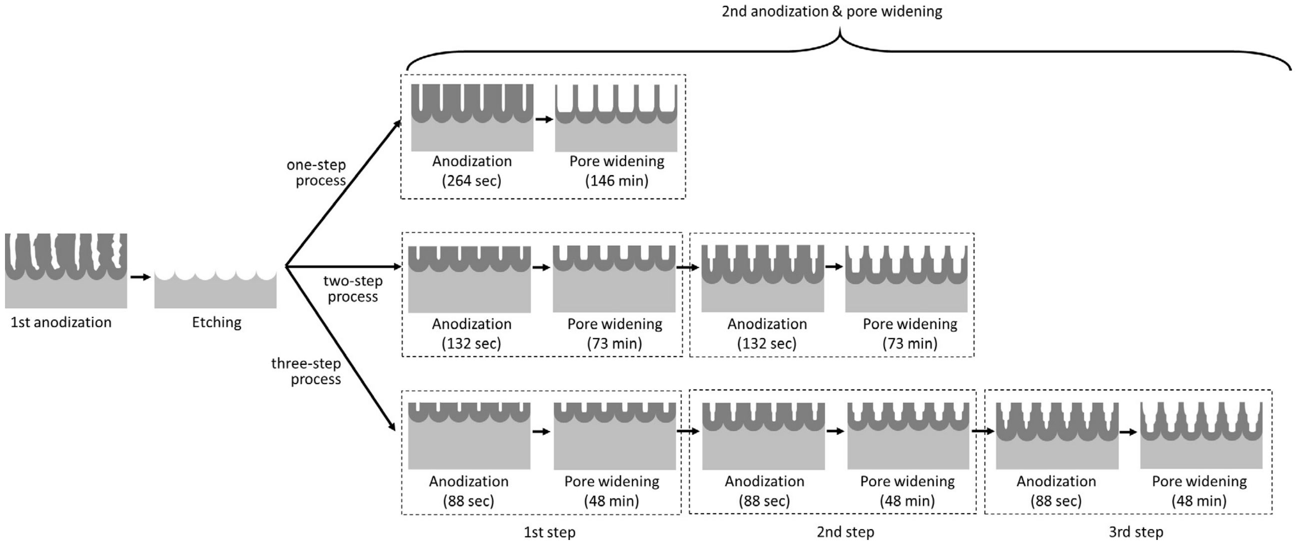

Fig. 1. Schematic diagram of fabrication process for controlling the shape of pore in AAO.

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