



## Full Length Article

# Facile fabrication of superhydrophobic hybrid nanotip and nanopore arrays as surface-enhanced Raman spectroscopy substrates



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## ABSTRACT

We demonstrate the fabrication of superhydrophobic hybrid nanotip and nanopore arrays (NTNPAs) that can act as sensitive surface-enhanced Raman spectroscopy (SERS) substrates. The large-area substrates were fabricated by following a facile, low-cost process consisting of the one-step voltage-variation anodization of Al foil, followed by Ag nanoparticle deposition and fluorosilane (FS) modification. Uniformly distributed, large-area ( $5 \times 5 \text{ cm}^2$ ) NTNPAAs can be obtained rapidly by anodizing Al foil for 1560 s followed by Ag deposition for 400 s, which showed good SERS reproducibility as using  $1 \mu\text{M}$  Rhodamine 6G (R6G) as analyte. SERS performances of superhydrophobic NTNPAAs with different FS modification and Ag nanoparticle deposition orders were also studied. The nanosamples with FS modification followed by Ag nanoparticle deposition (FS-Ag) showed better SERS sensitivity than the nanosamples with Ag nanoparticle deposition followed by FS modification (Ag-FS). The detection limit of a directly dried R6G droplet can reach  $10^{-8} \text{ M}$  on the FS-Ag nanosamples. The results can help create practical high sensitive SERS substrates, which can be used in developing advanced bio- and chemical sensors.

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## 1. Introduction

Surface-enhanced Raman spectroscopy (SERS) is a powerful spectroscopic analytical technique that is widely utilized in developing advanced bio- and chemical sensors to realize images of living cells [1,2], in vitro and in vivo diagnosis [3], food analysis [4], trace molecule detection [5] and so on. SERS is dominantly dependent upon the intensive electromagnetic field in the vicinity of metal or metal-decorated nanostructures due to their localized surface plasmonic resonance, which can dramatically amplify Raman scattering signals of target molecules absorbed on nanostructures [3]. Thus, for practical applications, one of the key research topics is to develop facile, low-cost methods to construct large-area substrates that are uniformly covered by high density plasmonic nanostructures (i.e. hot spots), which is the prerequisite for simultaneously guaranteeing the sensitivity and reproducibility of SERS signals [5–13]. To date, various nanostructured arrays (e.g. nanocone [11], nanorod with narrow gaps [8] and 3D hybrid nanostructures [5,6]) have been fabricated by using top-down

lithography (e.g. nanosphere-assisted lithography [11] and optical lithography [12]) and template-assisted technology (e.g. nanoimprinting [9] and electrodeposition [6,7]), which have made a great breakthrough in realizing the high sensitivity and reproducibility of SERS signals. However, top-down lithography is time-consuming and requires sophisticated equipment [10–12]; Meanwhile, template-assisted technology is restricted by available templates, which is always followed by complicated processing to obtain the highly sensitive nanostructures [5–9]. Thus, developing facile, low-cost methods to fabricate uniformly distributed, large-area plasmonic nanostructured arrays remains a challenge.

Another issue for SERS is that it needs an efficient way to bring the target molecules to the surface of plasmonic nanostructures [14]. For dilute aqueous solutions, nanostructures always need to be dipped into the solution for more than 8 h before detection to achieve uniform analyte absorption. The diffuse rate of analyzed molecules to the nanosurface is very slow (ca. 60 h/cm) [15]. To solve this problem, scientists have turned to the substrates own both SERS and superhydrophobicity [14–20]. The nanostructure not only can act as hot spots for SERS detection, but also enrich the analyte of a spherical droplet into a small area due to the concentration effect [19]. To simultaneously achieve these two functions above, it needs to skillfully design the nanostructure. To

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date, various SERS and superhydrophobic structures have been reported, such as nanotip or nanorod arrays [14], hybrid micro- and nanostructure [16,17], nanoflakes [18] and so on. However, each method still requires significant advancement in their fabrication techniques to realize the practical applications of SERS and superhydrophobic substrates.

Porous anodic alumina formed by electrochemical anodization is considered to be a good SERS-active substrate due to its advantages in terms of stability, low cost, operating convenience and technique compatibility [21–24]. However, in traditional anodization, it needs long time (>8 h) to obtain self-ordered nanodents on Al surface [25]. The conventional cylindrical alumina nanopore arrays are not the proper structure either for SERS [23] or superhydrophobic property [26]. In principle, alumina hybrid NTNPs should realize the both SERS and superhydrophobic functions after deposited with Ag nanoparticle and modified with low-free-energy fluorosilane (FS). First, the nanotips can excite intensive electromagnetic field and avoid the capillary effect due to the interrupted cell wall [23,26]. Second, the nanopores can provide a stable air-pocket to ensure superhydrophobic property [26]. However, the SERS performance of superhydrophobic NTNPs has not been reported. It is still a great challenge to fabricate NTNPs in a facile and rapid way.

The present study shows that superhydrophobic NTNPs with high SERS performance can be facilely, rapidly and economically fabricated by a designed process—one-step voltage-variation anodization of Al foils followed by Ag nanoparticle deposition and FS modification. The structural parameters of alumina NTNPs can be controlled by anodization time, and the one under 1560 s anodization followed by 400 s Ag deposition exhibited the highest SERS intensity. The preliminary study showed that this SERS-active structure can uniformly distribute in a large area ( $5 \times 5 \text{ cm}^2$ ), which leads to good reproducible SERS signals on the surfaces of different batches of samples. Finally, the SERS performance of the superhydrophobic NTNPs with different FS modification and Ag deposition orders were studied. R6G with a concentration of  $10^{-8} \text{ M}$  in a  $20 \mu\text{L}$  droplet can be rapidly detected on NTNPs with FS modification followed by Ag deposition.

## 2. Experimental

### 2.1. Reagents and materials

Highly pure (99.999%) aluminum foils with a thickness of 0.2 mm were used as starting materials (Cuibolin Nonferrous Metals Co., Ltd, Beijing, China). Analytical reagents were produced by Tianjing TianLi Chemical Reagents Ltd (China), including phosphoric acid ( $\text{H}_3\text{PO}_4$ , 85 wt%), chromium trioxide ( $\text{CrO}_3$ , 99 wt%), perchloric acid ( $\text{HClO}_4$ , 70–72 wt%). Ag targets (99.99%) were purchased from Thermo Fisher. The de-ionized water was produced by a pure water system.

### 2.2. Fabrication of hybrid nanotip and nanopore arrays

Al foils ( $50 \text{ mm} \times 50 \text{ mm} \times 0.2 \text{ mm}$ ) were firstly electropolished in a mixture of perchloric acid and ethanol ( $V/V = 1:4$ ) for 8 min (20 V,  $0^\circ\text{C}$ ). The electropolished Al foil was then placed in a custom-tailored electrochemical cell, where the Al foil was used as the anode and a platinum electrode was employed as a counter electrode. The distance of these two electrodes was fixed at 3.5 cm. Alumina hybrid nanotip and nanopore arrays (NTNPs) were fabricated by one-step voltage-variation anodization of Al foils in  $40^\circ\text{C}$  phosphoric acid solution, which was under violent agitation. Al foils was anodized at 25 V for 30 s, and then the anodization voltage linearly increases with the rate of  $0.5 \text{ V}/10 \text{ s}$  until current den-

sity ( $j$ ) reach the peak value of  $20 \text{ mA}/\text{cm}^2$ , after that the voltage exponentially decreased with the fixed  $j$  value. The anodization was stopped at the desired time.  $j$  was calculated by dividing the current values measured from the power supply system (IT 6874A, ITECH) by the anodized sample area. After reaction, anodized aluminium foils were rinsed with deionized water and then dried by nitrogen airflow. To obtain the SERS-active surface, Ag nanoparticles were uniformly deposited on the surface of alumina NTNPs at the rate of  $1 \text{ \AA}/\text{s}$  under  $3 \times 10^{-6} \text{ Pa}$  by a customized DE 400 electron beam evaporator (DE Technology Inc, China).

### 2.3. Fluorosilane modification

To obtain the superhydrophobic property, the as-prepared NTNPs without or with deposited Ag nanoparticles were placed, together with  $10 \mu\text{L}$  heptadecafluorodecyltrimethoxysilane liquid (Sigma-Aldrich Trading Co., Ltd., China), into a sealed glass container and then heated at  $120^\circ\text{C}$  for 2 h.

### 2.4. Characterizations

Top views of the as-prepared NTNPs with different Ag nanoparticle deposition durations were directly studied under high-resolution scanning electronic microscope (SEM, Nova NanoSEM 450, USA). Side views of the sample were obtained after sputtering a 15-nm thickness of Au layer on alumina NTNPs instead of Ag nanoparticle deposition. Water contact angles were measured at ambient temperature by an optical contact angle meter (Data-physics OCA20, Germany). The hemispherical reflection spectra were measured by a spectrophotometer (Perkin Elmer lambda 950, USA) equipped with an integrating sphere for wavelengths of 400–800 nm.

### 2.5. SERS measurement

For the samples without fluorosilane modification, the samples were immersed in identical  $1 \mu\text{M}$  R6G aqueous solution for 8 h to make sure the surface adsorbed a layer of R6G molecules. Subsequently, the samples were dried by nitrogen gas flow after rinsed with de-ionized water. For the samples with fluorosilane modification, droplets ( $20 \mu\text{L}$ ) with different R6G concentrations were directly deposited on the samples and the contrast sample. The droplet was evaporated at room temperature. Raman spectra were collected by a confocal Raman Spectrometer (Horiba Jobin-Yvon LabRAM HR Evolution) with a  $50\times$  objective lens and an excitation wavelength of 532 nm. The effect power of the laser source was  $2 \mu\text{W}$  at the surface of the samples, which had an average spot size of  $3 \mu\text{m}$  in diameter. The acquisition time was 1 s.

## 3. Results and discussion

### 3.1. Synthesis process of superhydrophobic NTNPs for SERS detection

The fabrication procedure for SERS and superhydrophobic NTNPs is shown in Fig. 1. Alumina NTNPs was firstly prepared by one-step voltage-variation anodization in high temperature phosphoric acid (Fig. 1a). The formation of NTNPs should be ascribed to skillfully utilize the co-effects of enhanced aluminum anodization and alumina etching in high temperature phosphoric acid electrolyte, voltage-variation procedure and the different chemical composition of anodic alumina. Firstly, compared with the conventional pore growth (using  $-4^\circ\text{C}$  phosphoric acid) [27], our adopted electrolyte ( $40^\circ\text{C}$  phosphoric acid) can simultaneously realize the fast aluminum anodization and good etching ability upon the alumina nanopore wall. Secondly, voltage-variation

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