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Aligned silver nanorod arrays for surface-enhanced Raman spectroscopy

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ABSTRACT

A convenient nanotechnique is used to place analyte molecules between closely spaced silver nanorods for investigating surface-enhanced Raman scattering (SERS). The route involves letting absorption of saturated $AgNO_3$ solution in the pores of the porous anodic alumina templates, followed by drying and decomposition of the salt at high temperatures. The silver nanorod arrays boast a high SERS enhancement and large dynamic range. The interrod-coupling-induced enhancement was attributed to the broadening of the plasmon resonance peak because the probability of the resonance covering both the excitation wavelength and the Raman peak increases with its width. The method will be useful in the development of plasmon-based analytical devices, specifically SERS-based biosensors.

1. Introduction

Surface-enhanced Raman scattering (SERS) is recognized as one of the most sensitive spectroscopic tools for high-sensitivity chemical and biological detection [1,2]. The fact that particle plasmon allows direct coupling of light to resonant electron plasmon oscillation has spurred tremendous efforts in the design and fabrication of highly SERS-active substrates in nanostructured films and metallic nanoparticles [3,4]. The most established substrates are the ones sprayed with Ag or Au colloids that yield intense SERS signals at certain local hot junctions [5,6]. However, a reliable, stable, and uniform SERS signal with large dynamic range cannot be easily achieved using this method. Theoretical studies have shown that localized plasmon modes created by strong electromagnetic coupling between two adjacent metallic objects in an array of nanostructures dominate the SERS response, and the effective Raman cross-section of a molecule placed between two metallic nanoparticles can be enhanced by more than 12 orders of magnitude [7,8]. Currently, the most studied approach is bulk solution-based biochemical detection using colloidal noble nanoparticles [9,10]. However, such substrates suffer from limited stability and reproducibility and in general, are not amenable to large-scale production of SERS-based sensors. In order to fabricate noble nanoparticle arrays with high SERS activity and improve the uniformity, lithographic techniques have been employed [11–14]. Although the potential of using SERS as a sensitive molecular sensing tool has been demonstrated, it is still very difficult to attain precise control of the gaps between the nanostructures on a SERS-active substrate in the sub-10 nm regime (necessary for intense SERS enhancement) by traditional lithographic techniques and nanofabrication methods [15,16].

Very recently, we have proposed a simple method to obtain hot geometries of the "tip/analyte/tip" arrangement [17,18]. In this technique, analyte molecules were placed between closely spaced silver-capped Si nanowires. It was found the silicon nanowires are less rigid, and gravity as well as van der Waals attraction cause bending and agglomeration of the Ag caps subsequently reducing the SERS intensity. Here, we present SERS measurements of molecules absorbed on silver nanorod arrays grown from porous anodic alumina (PAA) nanochannels. Because PAA membranes could protect silver nanorod arrays which are sealed in the pores, the hot geometries of the nanorod arrangement is potentially immune to contamination until they are ready for use.

2. Experimental

PAA membranes as templates were electrochemically grown in 0.4 mol/L phosphoric acid at 150 V using polished Al sheet

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(2×2 cm) with a thickness of 0.1 mm and a purity of 99.99%. The anodizing voltage was stepped up from zero using a linear potential scan at the rate of 0.2 V/s. And the temperature of electrolyte was maintained around 0 °C during anodization. The time of anodization was set to be 10 h. The porous template was immersed in saturated silver nitrate solution for about 30 min and heated slightly. Thus, the pores of the PAA membrane were filled with silver nitrate solution due to capillary interactions. After the excessive silver nitrate solution was wiped with filter paper, the PAA membrane was dried at 80 °C to evaporate the solvent. Then, the salt-filled template was heated at 500 °C for 30 min. The silver nitrate in the nanopores of the template decomposed into metallic silver and gaseous products. Finally, 1 mol/L KOH solution was used to remove partial of the PAA template and the aluminum substrate alike. The resulting nanorods were then washed repeatedly by distilled water and collected.

The morphology and chemical composition of the samples were determined using a FEG JSM 6335 field-emission scanning electron microscope (SEM) and an EDAX PV7715/89 ME energy-dispersive X-ray (EDS) detector.

For evaluation of the substrate Raman-enhancing capability, rhodamine 6G (R6G) 10^{-4}–10^{-7} mol/L water solutions were used. For allowing the molecule adsorption the substrates were maintained for 30 min in R6G solution and then were taken out and rinsed thoroughly. Raman measurements were performed on a Jobin–Yvon T64000 triple Raman system with the 514.5 nm laser line at room temperature. The probe area was ~10 μm in diameter with a 10 × objective lens and the incident power was 5 mW.

3. Results and discussion

Fig. 1 shows the schematic illustration of fabrication of the silver nanorod arrays. The process involved letting the absorption of saturated $AgNO_3$ solution in the pores of the PAA templates, followed by drying and decomposition of the salt at high temperatures. The pore diameters of the PAA membranes are in the range 150–200 nm. After the pores of the PAA membrane were filled with $AgNO_3$ solution due to capillary interactions, the $AgNO_3$ filled template was dried to evaporate the solvent. As a result, solid $AgNO_3$ adhered to the pore walls of the template. Then, the salt-filled template was heated at high temperature (500 °C). The $AgNO_3$ in the nanopores of the template decomposed into metallic silver and gaseous products. Finally, silver nanorod arrays were freed from the PAA template by partially dissolving the alumina membrane with alkaline treatment. It was also reported that silver nanotubes could be generated using this simple route [19]. The morphology of the resulting silver products depends strongly on the concentrations of the $AgNO_3$ solution precursor.

The surface morphology of the products shown in Fig. 2(a) was characterized using SEM, which demonstrated that arrays of vertically aligned cylindrical silver nanorods were obtained. The average diameter of these silver nanorods was about 200 nm, which agrees with the pore sizes of the alumina template. Some nanorods are bundled together. The phenomenon of nanorod aggregates can be explained by the irregularity of the individual nanorods as well as van der Waals attraction between them. According to the typical formation mechanism of silver nanorods, if the shape of nanorods is irregular, the centre of gravity of each

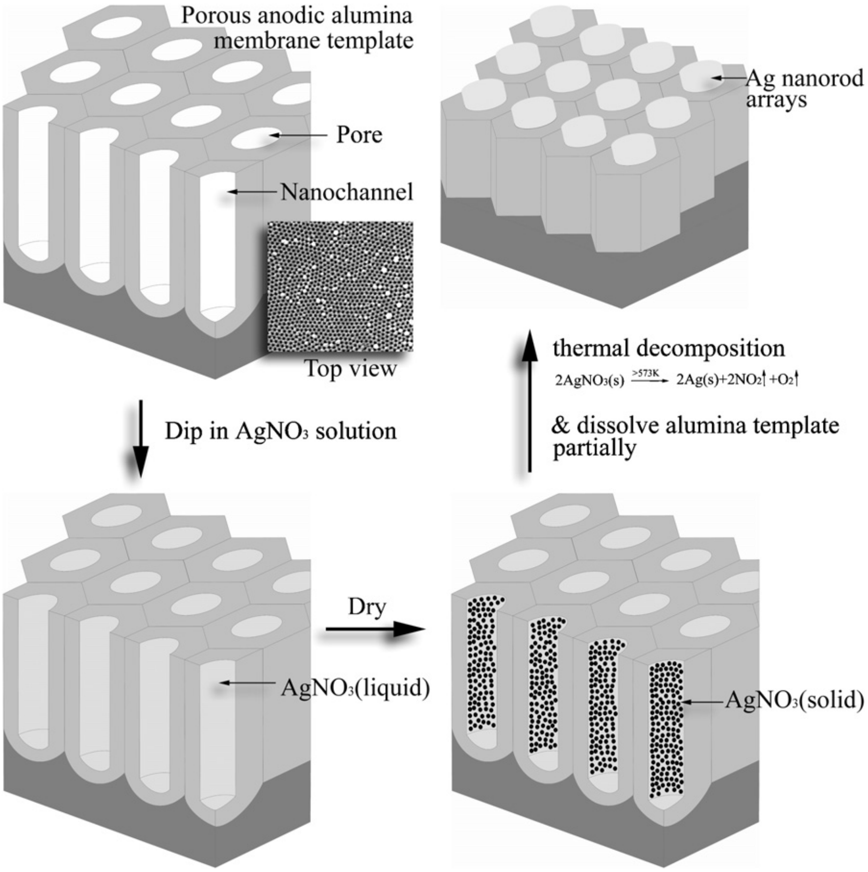

Fig. 1. Schematic illustration of fabrication of the silver nanorod arrays.