Atomic layer deposition of platinum thin films on anodic aluminium oxide templates as surface-enhanced Raman scattering substrates

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1. Introduction

Surface-enhanced Raman scattering (SERS) is one of the most powerful spectroscopic techniques [1,2] for high-sensitivity and nondestructive chemical and biological sensing [3,4]. The SERS effect is dominated by the localized electromagnetic field coupling between two adjacent metallic objects in a nano-array [5,6], and the effective Raman cross section of a molecule placed between two metallic nanoparticles can be enhanced dramatically [7]. Hence, preparation of ordered nanostructures with even plasmonic field distribution and ideal enhancement factors are the key issues [8]. We have recently developed a facile technique to obtain high-density hot-spots on SERS substrates using anodic aluminum oxide (AAO) as the template [9]. A continuous silver thin film is deposited on the self-organized AAO membrane by conventional direct-current (DC) magnetron sputtering to form ordered hexagonal island-like structures which possess excellent Raman-enhancing performance and high enhancement factors. However, nanostructured silver is easily oxidized and unstable in air thereby hampering wider applications. As an alternative, more stable noble metals such as gold and platinum can be a substitute. Considering our motivation of biological detection, platinum may be a good option [11] due to its almost total inertness to the chemical groups of biological matters. Among the various fabrication techniques, atomic layer deposition (ALD) is mature and suitable [12,13], especially with respect to the production of high-quality platinum thin films on an oxide surface [14].

ALD is a vapor phase method for thin films making use of sequential self-limiting surface reactions. As the gaseous precursor molecules reach the sample surface, a gas—solid chemical reaction occurs and ceases when reactants are exhausted, thereby allowing layer-by-layer deposition and precise thickness control of the atomic layer level. Owing to the independent reactions and inert gas saturation on the sample surface, films produced by ALD are usually conformal to the initial surface even on nanoporous materials [14]. Unfortunately, metals produced on an oxide surface tend to form clusters in lieu of a continuous film because of the higher surface energy of the metal film relative to the oxide surface. Consequently, many ALD cycles are needed to fabricate a continuous metal film and film conformality cannot be guaranteed [15]. Furthermore, the steric hindrance effect caused by ligands of the organometallic precursor binding to oxide surface can exacerbate the situation [16]. Recently, plasma platinum ALD using...
(methylcyclopentadienyl)-trimethyl platinum (MeCpPtMe3) and oxygen plasma has been developed to produce continuous platinum thin films [17]. In this work, continuous platinum thin films with highly ordered nano-islands are deposited on AAO templates by the plasma ALD technique. Theoretical calculation and experiments are conducted to elucidate the enhancement mechanism and determine the actual enhancement factor. The long-term reliability of the materials is also assessed.

2. Experimental details

All chemicals including (methylcyclopentadienyl)-trimethyl platinum (MeCpPtMe3), rhodamine 6G (R6G), adenine, and adenosine were analytical grade purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without any further purification. All the solutions were prepared with demineralized and filtered water.

The AAO templates were fabricated by anodic oxidation by varying the DC voltage at 10 °C. An ordered nanopore structure was produced by a two-step anodizing process using optimized parameters reported previously [9,18]. The Pt films were deposited on an ALD instrument with an inductively-coupled plasma (ICP) source at 300 °C. The reactor was evacuated to less than 10⁻³ Pa by a turbomolecular pump backed by a mechanical one. The Pt precursor (98% pure MeCpPtMe3) was vaporized at 70 °C and introduced into the reactor. Deposition was carried out at an oxygen flow rate of 20 sccm (working pressure of about 10⁻² Pa) for 300 cycles (100 W plasma power for 1 s for each cycle).

FE-SEM (JEOL, JSM-6335F) and AFM (Veeco, DI nanoscope IIIa) were conducted to investigate the structure of the AAO and prepared samples. Raman scattering was performed on a Renishaw inVia micro-Raman system using the 633 nm laser line at 20 °C. The laser spot was about 1 μm in diameter and there was a 100× objective lens. The performance of the SERS substrate was assessed by using R6G as the molecular probe at an incident power of 0.04 mW for a cumulative time of 50 s. The Raman signals from adenine (minimum 99% purity) and adenosine (minimum 99% purity) molecules were measured at under 0.2 mW for 40 s. The 10⁻⁵ M aqueous stock solution of R6G (99% pure) was prepared for SERS measurement. The substrates were immersed in the solution for 30 min to enable adsorption of molecules, taken out, and rinsed thoroughly with deionized water. The acquisition time and laser power used for the R6G Raman spectra were the same for both the silver and platinum films for the proper comparison and the platinum films were stored for 90 days to study the long term stability. The spectra were taken from different sites on the surface and the average intensity and standard deviation (SD) were calculated to ensure good statistics and reproducibility.

The local electromagnetic fields were calculated using the commercial FDTD software (FDTD Solutions 6.5, Lumerical Solutions Inc.). The model consisted of a periodic structure with six hexagonally arranged cones. The bottom radius of the cone is 30 nm and the top hemisphere has a radius of 20 nm. The 633 nm laser was assumed to impact the sample surface normally.

3. Results and discussion

The typical morphology of the AAO template prepared at 40 V is depicted in Fig. 1a. The FE-SEM image is taken at a 30° tilt to illustrate the hexagonal structure of the template. The perfect self-organized growth during anodic oxidation provides good control of

![Fig. 1](image-url). (a) FE-SEM image of the representative AAO template at a 30° tilt, (b) FE-SEM image of the platinum-based SERS substrate, (c) AFM pattern of the as-prepared SERS substrate and (d) Contour of the near-field electromagnetic distribution of a model structure. The scale bar is 100 nm.
the nanostructure arrangement but only occurs at certain anodic voltages. Furthermore, the hexagonal stricture expands and shrinks as the anodic voltage is varied [9]. In our experiments, 40 V is used and the length of the hexagonal side is about 60 nm.

The FE-SEM image of the platinum film deposited by using 300 ALD cycles is presented in Fig. 1b. The image quality of the platinum film is much better than that of the AAO template due to less electron accumulation on the surface due to better electrical conductivity. The orderly island-like hexagonal structure is demonstrated clearly and the island diameter is about 40 nm. The surface morphology of the film with the island-like structures is shown in the AFM image in Fig. 1c. The 3D pattern is tilted to show the details of the island-like structure which resembles a cone with a rounded tip. The tip diameter is about 40 nm and the cladding diameter is about 60 nm. An ideal rounded tip cone array model is constructed for the FDTD simulation which has been verified to be a very useful tool for studying electromagnetic properties of metallic nanostructures. To evaluate the local electromagnetic fields at an excitation wavelength of 633 nm, FDTD calculation is performed and the contour plot of the electromagnetic near-field distribution is presented in Fig. 1d. Orderly hot spots exist near the interstitial areas of the platinum cones. The largest enhancement factor is calculated to be $1.12 \times 10^8$ using the formula $EF = \frac{E_{loc}/E_0}{C_{loc}/C_0}$, which shows that the enhancement factor (EF) varies with the fourth power of the local electric field intensity ($E_{loc}$). Here, the gap between the cones contributes primarily to the strong local electric field enhancement thereby leading to excellent SERS performance.

To experimentally evaluate the Raman performance, a $10^{-5}$ M aqueous stock solution of R6G is used and the Raman spectra are shown in Fig. 2. A million fold enhancement estimated from the reported formula [9,19] is observed under these conditions. The 633 nm excitation wavelength is chosen to reduce fluorescence interference caused by fluorescence quenching and enhancement [20]. The characteristic peaks of R6G can be observed from the plots. The salient peaks at 1365, 1510, 1578, and 1652 cm$^{-1}$ can be assigned to the symmetric modes of in-plane C–C stretching vibrations. The experimental results are consistent with the simulation results described previously, suggesting a high density of hot spots in the hexagonal island-like structures. Owing to the chemical inertness of Pt, the SERS capability can be maintained for 90 days. The inserts in Fig. 2 show the average intensities measured from the fresh deposited substrate as well as that after storage in air for 90 days. The minor degradation may be due to adsorbed contaminants from air due to the large surface energy of the nanostructures, but nonetheless, the durability is much better than that observed from silver after the same storage period.

To demonstrate the potential applications of the platinum-based SERS substrates, adenine, one kind of deoxyribonucleic acid (DNA) bases, is used as the target molecule. It does not exhibit appreciable one-photon absorption at 633 nm excitation and therefore has a very low fluorescence background and minimal interference. The SERS spectrum acquired from $10^{-5}$ M adenine shown in Fig. 3 is generally in agreement with those reported earlier [21] showing characteristic Raman lines at 739 cm$^{-1}$ and 1339 cm$^{-1}$ corresponding to the purine ring breathing mode and CN stretching mode, respectively. The ultra-sensitive detection of adenine suggests that monitoring of DNA sequencing on the single-molecule level is possible on this engineered substrate after further optimization to attain higher detection limitation or detecting the mismatch of DNA sequences after the integration to a chip-based platform [22,23]. For further confirmation, adenosine is chosen as another target molecule because of the important role played by adenosine triphosphate (ATP) molecules in biological energy transfer reactions. The SERS spectrum obtained from $10^{-5}$ M adenosine adsorbed on the platinum-based substrate is displayed in Fig. 3. Compared to the adenine spectrum, the peaks of the purine ring breathing mode and CN stretching mode shift to 724 cm$^{-1}$ and 1328 cm$^{-1}$ respectively. It may be attributed to alteration in the adsorbed group. In addition, the more complex molecular structure of adenosine and concomitant steric hindrance effect should be considered in the molecule adsorption process. It is believed that the reduced intensity observed from some of the Raman peaks is due to this effect and more work is being done in our laboratory for further clarification.

4. Conclusion

A platinum thin film is deposited on the AAO template by ALD to produce an ordered hexagonal structure with SERS characteristics. The FDTD calculation indicates that the platinum hexagonal structure gives rise to high SERS signals due to the high density of hot spots and it is verified experimentally. The platinum-based SERS substrate retains the excellent characteristics even after storing in

![Fig. 2](image-url)  
Fig. 2. SERS spectra obtained from $10^{-5}$ M R6G absorbed on the platinum island-like hexagonal structures immediately and after 90 days. The insert compares the SERS substrates. All the spectra and data were obtained at 633 nm laser excitation for an integration time of 50 s and a laser power of 0.04 mW.

![Fig. 3](image-url)  
Fig. 3. SERS spectra of $10^{-5}$ M adenine and $10^{-5}$ M adenosine absorbed on the platinum-based SERS substrates. All the spectra and data were obtained at 633 nm laser excitation for an integration time of 40 s and a laser power of 0.2 mW.
air for 90 days. The substrate can thus be used reliably in trace detection of biological molecules.

Acknowledgments

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References