Growing Silver Nanoparticles on Porous Alumina Templates *In Situ* to Produce Improved SERS Substrates

Benjamin Revard, Georgie Tech, IREP 2010 Fellow
Faculty Advisor: Dr. Vladimir Tsukruk Graduate Mentor: Maneesh Gupta

Introduction

Current events have highlighted the need for chemical and biological sensors with high sensitivity. Applications exist in the areas of biological sensing, trace chemical and explosives analysis, and monitoring nanoscale chemical and biological phenomena.[1] SERS (surface enhanced Raman spectroscopy) has proven to be a good method to obtain desirable detection limits, allowing even single molecules to be detected.[3]

A challenge in the application of SERS has been to develop substrates which provide a large enough enhancement of the Raman signal to provide the desired limit of detection. The objective of this study is to create a three-dimensional substrate which will maximize the SERS signal by adjusting the size and density of silver nanoparticles on a porous alumina template. Previous attempts to create a similar SERS substrate had focused on attaching silver nanoparticles grown in solution to alumina templates.[1] However, this method did not result in a high enough density of silver nanoparticles on the pore walls of the templates to produce a good SERS enhancement. In this study, we attempt to achieve a higher density of silver nanoparticles in the template pores by synthesizing them *in situ*.

Procedure

We first used electroless deposition to place silver seeds on the walls of the porous alumina templates. The alumina templates were 13 mm in diameter and 60 microns thick, and contained continuous vertical pores approximately 200 nm in diameter. They were first placed in a 0.02 M $SnCl_2$ and 0.01 M HCl solution for two minutes. They were then gently rinsed with pure water, followed by ethanol, and dried at 70°C. After the templates were completely dry, which usually required two to four minutes of drying time, they were then placed in a 0.02 M $AgNO_3$ and 0.01 M HCl solution for two minutes. Again the templates were rinsed with pure water and ethanol and dried.[2] This process was repeated two, three, or four times, depending on the desired density of silver seeds on the alumina templates. The silver was adsorbed to the walls of the porous alumina templates and reduced by the tin according to the reaction

$$Sn^{2+} + 2Ag^{1+} \rightarrow Sn^{4+} + 2Ag(s)$$

Overgrowth solutions of 0.1 M CTAB, 0.1 M $AgNO_3$, and 0.1 M ascorbic acid were produced by first adding the CTAB, then the silver nitrate, and then the ascorbic acid to the solution. To overgrow the silver seeds, the alumina templates were placed in this solution overnight at ambient conditions.

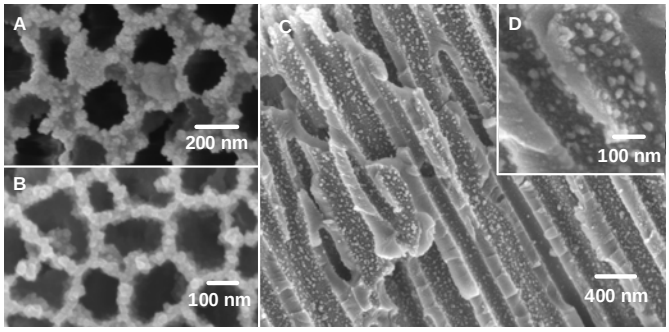

Figure 1. SEM images of silver nanoparticles on an alumina template. A) Silver nanoparticles on the top side of the template. B) Silver nanoparticles on the bottom side of the template. C) Cross section of alumina template showing silver nanoparticles on pore walls. D) Close-up of cross-sec

Results and Discussion

The alumina templates were dark brown after the silver seeds had been deposited on them, but the color lightened significantly after soaking overnight in the overgrowth solution. We found that the templates which had had silver seeds deposited on them four times provided the best density of nanoparticles after the overgrowth had been carried out. As can be seen in Figure 1, this method produced a much higher density of silver nanoparticles on the pore walls of the template than the previous method of first growing nanoparticles in solution and then depositing them on the template. This provides a much higher density of hot spots where the Raman signal can be drastically enhanced. In addition, we achieved nearly uniform coverage of the nanoparticles throughout the length of the pores, and the nanoparticles are not simply spherical, but have roughened shapes, which further enhances the Raman signal.

Conclusions

Silver nanoparticles were grown *in situ* on the walls of porous alumina templates to form a SERS substrate. A high density and uniform coverage of nanoparticles was obtained, which was the goal of this study. Future work includes obtaining UV-Vis spectroscopic data and measuring SERS activity for these samples. This data can be used to tailor nanoparticle synthesis to create future substrates with even better SERS signal enhancement properties.

References and Notes

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