Field Enhancement Dependence on the Shape and Size of Au Nanoparticles in Surface-Enhanced Raman Spectroscopy-Active Substrates

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Introduction

Surface-Enhanced Raman spectroscopy (SERS) has recently got a lot of attention due to its rapid identification of chemical, bacterial samples and single molecule detection. Various studies on nanostructures have been reviewed [1]. The fabricated nanostructures for both bottom-up and top-down approaches have been reported. And, the degree of Raman enhancement is strongly dependent on the morphology of formulated nanostructures. Recently, a top-down approach for the fabrication of SERS-active substrate was proposed [2]. However, the expensive substrate, equipments and complicated process are needed. Therefore, a low cost, environment friendly and simple fabrication for SERS-active substrates will be of great interest for basic and clinical researchers as well as for biotechnologies. In this study, we experimentally and computationally study the local field enhancements of nanoparticles on hydrothermally roughened SERS-active substrates [3], where application of the fabricated samples in identification of Rhodamine 6G (R6G) is discussed.

Computational Model

The Fig. 1(a) shows the three-dimensional (3D) view of the gold-coated nanoparticular structure, where the 3D finite-difference time-domain (FDTD) numerical simulation is adopted to investigate the field enhancement of substrates. The 3D FDTD method solves a set of Maxwell's equations by first discretizing the equations via central differences in time and space. Then, we base on Yee's mesh and the electric and magnetic field components at points on a grid with grid points to solve these equations. The Maxwell's equations are iteratively solved in a leapfrog manner, alternating between computing the E and H fields at subsequent $\Delta t / 2$ intervals [4], as shown in Fig. 2.

Results and Discussion

For chemical sensing, the hydrothermally roughened substrates are treated with aqueous solutions of $10^{-4}$ M R6G, where AFM images of titanium thin films treated under hydrothermal conditions for 12 h treatment duration as shown in Fig. 1(b). Fig. 3 shows the characteristic Raman vibrational modes of R6G immobilized on the substrate with or without hydrothermal treatment. The substrate with hydrothermal treatment shows larger intensity than that without hydrothermal treatment due to the roughness on the surface. Through using the FDTD simulation, the evaluation of electric field on the substrates is carried out by directing light with a wave length of 633 nm. Notably, the nanosensor also can be fabricated by other synthesis methods to achieve different shape of nanoparticles. Therefore, we further consider cubic and pyramid shapes of nanoparticles. The 3D simulation results show that the electric field (Ex) enhancement of cube is larger than that of spherical and pyramid shapes, as shown in Fig. 4. Then, we consider different samples which are gold nanoparticle, gold nanocage and gold/silver alloy (from left to right) for spherical, cubic and pyramidical shapes, as shown in Fig. 1(c). From the results of Fig. 4, the Au/Ag alloy is adopted for spherical shape. For pyramid, the nanocage or metal alloy is the same. The corresponding distributions of electric field are shown in Figs. 5, 6 and 7, respectively.

Conclusions

In conclusion, we have successfully prepared SERS-active substrates with low background for the detection of both Rhodamine 6G and Staphylococcus aureus. The enhancement can be controlled by tuning the surface roughness of the substrates through varying treatment duration. Through the FDTD simulation, the field enhancement of spherical and cubic shape nanoparticles can be enhanced by using Au/Ag alloy and nanocage samples, where the different shape of nanoparticles also can be fabricated by other synthesis method for local field enhancement in diverse nanosensor applications.

Acknowledgment

This work was supported in part by Taiwan National Science Council (NSC) under Contract NSC-97-2221-E-009-154-MY2.

References

Figure 1. (a) A schematic plot of the 3D view of simulated structure. (b) The AFM images of titanium thin films treated under hydrothermal conditions for 12 h treatment durations. (c) Gold nanoparticle, gold nanocage and gold/silver alloy (from left to right) for spherical, cubic and pyramidal shapes, respectively.

Figure 2. The simulation procedure of solving the Maxwell’s equations.

Figure 3. The Raman spectra for Rhodamine 6G (10^{-4} M) immobilized on hydrothermally untreated (blue) and treated (orange) substrates.

Figure 4. The plot of electric field enhancement factor versus different samples.

Figure 5. The top view of electric field distribution with spherical shape of (a) Au nanoparticle, (b) Au nanocage and (c) Au/Ag alloy, respectively.

Figure 6. The top view of electric field distribution with cubic shape of (a) Au nanoparticle, (b) Au nanocage and (c) Au/Ag alloy, respectively.

Figure 7. The top view of electric field distribution with pyramidal shape of (a) Au nanoparticle, (b) Au nanocage and (c) Au/Ag alloy, respectively.