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Investigation of Raman enhancement in hydrothermally roughened SERS-active substrates

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ABSTRACT

In this work, we study surface enhanced Raman spectroscopy (SERS) active substrates for the detection of Rhodamine 6G. To examine the electromagnetic enhancement, we apply the finite-difference time-domain (FDTD) algorithm to analyze the structures by solving a set of coupled Maxwell's equations (Ampere's Law and Faraday's Law) in differential form. The field enhancements are thus investigated in the visible regime with the wavelength of 633 nm. In our experimental measurement, the surface enhanced Raman scattering signals from the surface of substrates with 12-hour treatment and without treatment are performed and compared. Through the three-dimensional (3D) FDTD calculation, we find that the hydrothermally 12-hour treated samples possess significantly vertical variations of surface and thus have relatively larger field enhancement than those without treated. Consequently, it implies a strong positive effect on the surface enhancement which is consistent with the measured intensity.

1. Introduction

Surface enhanced Raman spectroscopy (SERS) has recently attracted a great deal of attention for rapid identification of chemical samples and molecules detection [1,2]. However, expensive substrate and complicated process should be faced. In this work, we study a low-cost and environmentally friendly substrate using hydrothermal synthesis [3]. Sample fabrication is carried out from high-temperature aqueous solution at high pressures. The SERS-active substrate is used for identification of Rhodamine 6G (R6G) successfully. Through the finite-difference time-domain (FDTD) method [4–6], compared with measured intensity, we find that the degree of Raman enhancement strongly depends on the morphology of nanostructures. The measured surface enhanced Raman scattering signals from the surface of substrates with 12-hour treatment are significantly larger than that of without treatment due to significantly rough and wide variation in structural surface. In Section 2, we brief the fabricated SERS-active substrate and state the computational model. In Section 3, we present the results and discussion. Finally, we draw the conclusions.

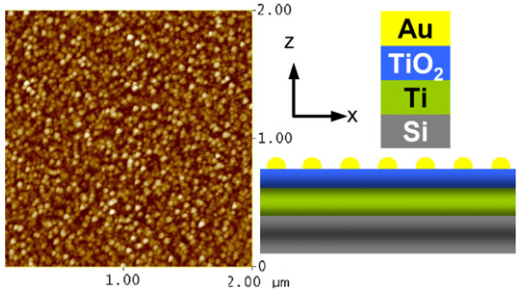

Fig. 1. The left photo is the AFM image of the fabricated titanium thin film. The right plot shows the FDTD simulated substrate.

2. The SERS structure and computational model

The left photo, as shown in Fig. 1, shows the atomic-force microscopy (AFM) image of the titanium thin film treated under the hydrothermal condition for a duration of 12-hour treatment [3]. Under the condition, titanium is oxidized to TiO_x in the initial hydrothermal stage. Prolonged treatment will let the TiO_x layer be dissolved, re-crystallized and grown into a nanostructured layer. The surface roughness varies with various treatment durations. The right lower plot of Fig. 1 shows the cross-section view of gold-coated nanoparticular structure for the FDTD simulation, where the upper plot shows each layer's information.

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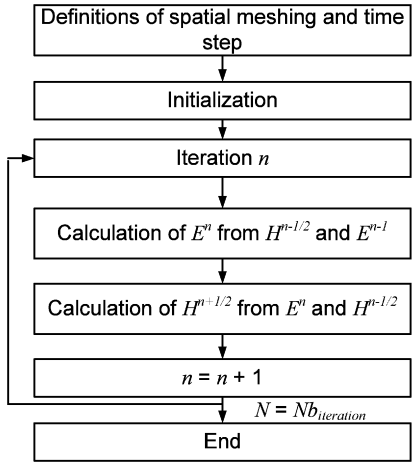

Fig. 2. The FDTD simulation procedure.

Numerical simulation using a 3D FDTD method is conducted to investigate the local field enhancement of substrate [4–6]. The Maxwell's curl equations in linear, isotropic, nondispersive, lossy materials are:

$$\frac{\partial B}{\partial t} = -\nabla \times E, \tag{1}$$

$$\frac{\partial E}{\partial t} = -\nabla \times \frac{J}{\epsilon} + (\mu\epsilon)^{-1} \nabla \times B, \tag{2}$$

$$\nabla \cdot E = \frac{\rho}{\epsilon}, \tag{3}$$

$$\nabla \cdot B = 0, \tag{4}$$

where E and B are the electric and magnetic fields, respectively, ϵ and μ are permeability and permittivity, respectively. For a globally defined curvilinear space, Maxwell's equations are easily implemented in their differential form, where Faraday's law is Eq. (1) and Ampere's law is Eq. (2).

The FDTD method solves Maxwell's equations by first discretizing all equations via central differences in time and space. Then, based upon a 3D Yee's mesh and components of the electric and magnetic fields at points, the discretized spacing in the x, y, and z directions adopted in our simulation are $\triangle x = 0.01$ um, $\triangle y = 0.01$ um and $\triangle z = 0.01$ um, where the time step $\triangle t$ is 0.0004 and the time duration T is 3 in units of femtoseconds. The discretized equations are iteratively solved in a leapfrog manner, alternating between computing the E and H fields at subsequent $\triangle t/2$ intervals, as shown in Fig. 2. Notably, we employ the perfectly matched layer as the simulation domain boundaries in which both electric and magnetic conductivities are introduced in such a way that wave impedance remains constant, absorbing the energy without inducing reflections.

3. Results and discussion

For chemical sensing, the hydrothermally roughened substrate is treated with aqueous solutions of 10^{-4} M R6G. Fig. 3 shows the measured characteristic Raman vibrational modes of R6G immobilized on the substrate with and without hydrothermal treatments are examined. The substrate with hydrothermal treatment shows larger intensity than that without hydrothermal treatment due to the roughness on the surface. The estimation of local electric field on the substrate is carried out using 3D FDTD simulation, where a directing light with the wavelength of 633 nm is considered. Without loss of generality, the effect of vertical variation of surface on the electric field (E_x) enhancement is observed, as shown in Fig. 4.

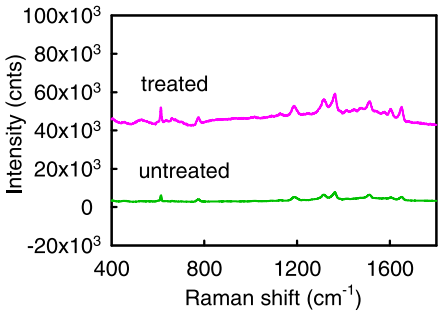

Fig. 3. The Raman spectra of the sample immobilized on hydrothermally untreated (green) and treated (pink) substrates. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

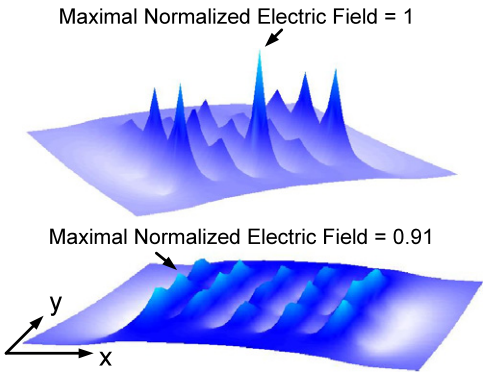

Fig. 4. The upper and lower plots show the FDTD simulated electric fields of the examined substrate with 12-hour and without hydrothermal treatment, respectively. The matrix size of particles is 3×5 accordingly to an approximately periodical assumption of the simulated structure; the simulation domain in the x–y plane is 0.4 um $\times$ 0.2 um.

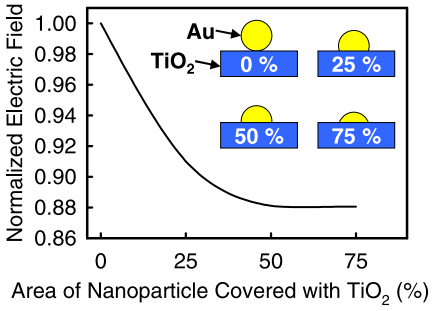

Fig. 5. The plot of normalized electric field versus the area of particles covered with TiO_2.

The gold-coated nanoparticular structure with hydrothermal treatment (upper plot) has larger electrical field, due to relatively rough surfaces, than that without hydrothermal treatment (lower one), according to Beckmann–Kirchhoff theory [7]. Further, the electric field of different nanoparticular area with TiO_2 is further evaluated. The results of this study show that the local field enhancement is decreased as the nanoparticular area covered by TiO_2 is increased, as shown in Fig. 5.

4. Conclusions

We have studied new SERS-active substrates for the identifications of Rhodamine 6G. This low-cost and environmentally friendly substrate is mainly using the hydrothermal synthesis technique. The computational estimation of local field enhancement using

FDTD method has confirmed the detected large intensity which indicates a clear view of such enhancement is resulted from vertical variations of the grown film. The file enhancement of substrates could be enlarged by roughening the surface and have less area covered with TiO_2 which enabled rapidly to identify chemical species.

Acknowledgement

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