A semi-colloidal substrate for surface enhanced Raman scattering

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ABSTRACT

In this work, we utilize the electrolysis effect to prepare a semi-colloidal substrate for surface enhanced Raman spectroscopy (SERS) applications in which the nanoparticles created on the anode surface act as an active medium for SERS. The experiments carried out with copper (Cu) as the electrode and Rhodamine B (RhB) as the electrolyte. The measured enhancement factor ($EF$) of the Raman peaks of RhB is more than five orders of magnitude. The proposed method has some key advantages: it is a very simple and low cost technique and also can be used in real time since it is a quite fast process.

Keywords: Surface enhanced Raman spectroscopy, semi-colloidal substrate, electrolysis, real time SERS substrate

1. INTRODUCTION

Preparing an appropriate surface enhanced Raman scattering substrate due to its importance in research laboratories and industries has been a central subject since the SERS was introduced in the mid-1970s. Since then different kinds of SERS substrates were developed like the assembly of colloidal nanoparticles in two-dimensional and 3-dimensional configurations, patterned substrates fabricated by nano-scale fabrication techniques such as electron beam lithography (EBL), focused ion beam (FIB), scanning probe lithography etc. Generally, all these substrate building methods can be classified in two different categories; bottom-up methods, and top-down methods.

Although it is a time consuming process and appropriate for large scale production, synthesis of colloidal nanoparticles which is known as a bottom-up method, is straightforward. However potential aggregation of the nanoparticles over the substrate is a significant disadvantage of this method. On the other hand, patterning of the substrate which is known as a top-down method, provides means of adjusting the uniformity and the inter-particle distance assuring the uniformity in enhancement factor, and absence of particles aggregation problem. Although it is repeatable, it is costly and time consuming, and much more complicated process which requires high-tech fabrication facilities.

Synthesis of nanoparticles by electrolysis which is the result of reduction and oxidation on the cathode and anode respectively, became popular recently. This is a bottom-up method, and considered for synthesis of colloidal nanoparticles for applications in the inkjet printing, SERS etc. Compared to most of the other synthesis methods of colloidal nanoparticles, this is a simple and economical method, and usually one needs a solution as an electrolyte that contains the ions of nanoparticles of interest. In particular, electrochemical method is one of the simplest way of producing copper oxide nanoparticles which is discussed in detail in the literature. In this work, we utilize the electrolysis effect to prepare a semi-colloidal substrate for SERS applications in which the nanoparticles created on the anode surface act as an active medium for SERS. The experiment carried out with copper (Cu) as the electrode and Rhodamine B (RhB) as the electrolyte. The measured enhancement factor ($EF$) of the Raman peaks of RhB is more than five orders of magnitude. The $EF$ versus time was also studied, which for 90 seconds electrolysis we obtained the maximum enhancement on the Raman peak of 1509 cm$^{-1}$. In addition to the enhancement factor, the proposed method has some key advantages: it is a very simple and low cost technique and also can be used in real time since it is a quite fast process.
2. EXPERIMENTAL SETUP

In order to perform the electrolysis experiment, 3 electrodes have been placed inside a 3 mL quartz cuvette in which two of them are parallel while the third one is perpendicular to these two electrodes, as illustrated in Fig. 1. The electrode from which the Raman signal was recorded is the anode while two other ones are used as the cathode. The applied voltage to the electrodes was 32 V.

Raman spectrum was recorded by a Raman probe made by InPhotonics Inc. And the other parts of the system are a QEpro spectrometer and an infrared laser source of 785 nm, both made by Ocean Optics Inc. The quartz cuvette was located in front of the Raman probe and the back scattered Raman signal was recorded from the surface of the anode electrode as shown in Fig. 1. The photograph of the whole set-up is illustrated in Fig. 2.
3. EXPERIMENTAL RESULTS

Initially, to investigate the SERS enhancement on the copper anode surface, we placed 3 copper electrodes inside a quartz cuvette of filled with RhB of 5 µM then applied a 32 V DC signal. In order to study the electrolysis effect on the Raman spectrum of RhB, the back scattered Raman spectrums from anode surface were recorded as a function of time. The enhancement factor \( EF \) of the recorded Raman signals is calculated according to:\textsuperscript{10} \[ EF = \frac{I_{\text{SERS}}}{I_{\text{ref}}} \times \frac{C_{\text{ref}}}{C_{\text{SERS}}} \], where \( I_{\text{SERS}} \), \( I_{\text{ref}} \), \( C_{\text{ref}} \) and \( C_{\text{SERS}} \) correspond to recorded Raman signal intensity from the SERS substrate, intensity of the reference Raman signal, concentration of the reference sample, and concentration of the SERS sample respectively. In order to obtain the optimum required time for electrolysis -to get maximum \( EF \)- we recorded the Raman spectrum at various electrolysis times. The recorded spectrums from Cu electrode (anode) surface and also the variation of \( EF \) for the Raman peak of 1509 cm\(^{-1}\) are shown in Fig. 3. As it is clear from this figure, even for 30 seconds electrolysis, the anode surface functions as a SERS active substrate as the Raman \( EF \) reaches above four orders of magnitude. The maximum \( EF \) (roughly \( 1.5 \times 10^5 \)) occurred at 90 seconds electrolysis then it started to reduce gradually for further electrolysis which after ten minutes of electrolysis time the \( EF \) decreased to almost fifty percent of the maximum value. These results are discussed in detail in the next section.

![Figure 3. EF of 5 µM RhB variation for different electrolysis times. For electrolysis time of 90 seconds the EF for the Raman peak of 1509 cm\(^{-1}\) reaches the maximum value of above 5 orders of magnitude. Reference spectrum was recorded from RhB of concentration of 100 mM in a second.](image)

The substrate \( EF \) uniformity for the Raman peak of 1509 cm\(^{-1}\) was quantified by calculating the \( EF \) on 6 random spots through a roughly 1 cm\(^2\) area of the Cu anode surface after 90 seconds electrolysis. The \( EF \) variation through these spots had a relative standard deviation (RSD) of roughly 11.7 percent. The spectrums of these spots and also the \( EF \) are shown in Fig. 4. A uniform \( EF \) was expected from the surface due to uniform current density on the surface which leads to uniform nanoparticles production on the substrate.

4. SURFACE ANALYSIS AND SIMULATION RESULTS

In order to have a better understanding of the Raman enhancement on the copper anode surface, we recorded the scanning electron microscopy (SEM) images of the substrates. The recorded SEM images show the production of copper oxide nanoparticles of the size of a few hundred nanometers. As it is shown in Fig. 5, at ninety seconds electrolysis the nanocubes size ranges from 30 nm to 150 nm with average size of 100 nm. However, at five minutes electrolysis, the nanocubes size ranges from 50 nm to 420 nm with average size of 300 nm.

The production of copper oxide nanoparticles on the anode surface can be explained by the tendency of copper to oxidation. Since the copper anode try to donate electrons and to form \( Cu^{2+} (Cu \rightarrow Cu^{2+} + 2e^-) \), there are \( Cu^{2+} \) cations on the anode surface and in the electrolyte. Some of these cations contribute in the reduction
process to produce Cu nanoparticles ($Cu_{2+} + 2e_\rightarrow Cu$) and some others contribute in the copper oxidation process ($Cu_2O, CuO$, etc). In this experiment the growth of the copper oxide nanoparticles is a fast process that in a few minutes the nanoparticles size reaches to about 400 $nm$ (see Fig. 5), and these particles are responsible for enhancing local electric field for SERS applications.

Later, we used FDTD technique to simulate the surface Plasmon resonance (SPR) wavelength for different nanoparticle sizes on the copper surface to explain the nanoparticle size effect on the $EF$. For this purpose, we selected a realistic collection of particles as shown with the dashed squares in Fig. 5. For the ninety second run simulations, we selected the $1 \mu m \times 1 \mu m$ area with nanocubes size ranging from 80 $nm$ up to 150 $nm$, while for five minutes run simulation, we selected the $2 \mu m \times 2 \mu m$ area with nanocubes size ranging from 90 $nm$ up to 350 $nm$. The nanoparticles distribution and simulation results for both cases are shown in Fig. 6. As it is clear from this figure, the extinction cross section for the case of ninety seconds electrolysis has the resonance wavelength of 790 $nm$, while for the case of five minutes electrolysis this resonance wavelength is 1015 $nm$. This difference in resonance wavelengths for two cases affects the enhancement factor. Since the substrate is excited with 785 $nm$ laser source, the substrate with resonance wavelength of closer to the excitation wavelength will have better enhancement factor on the SERS. In a nutshell, since, increasing the electrolysis time leads to increment in nanocubes size, and consequently the red shift in resonance wavelength, the reduction in SERS $EF$ is justifiable.
Figure 6. a) electric field amplitude distribution at 50 nm above the surface at SPR resonance of 790 nm for the case of ninety seconds electrolysis, b) the extinction cross section of this assembly of nanocubes as a function of wavelength, c) electric field amplitude distribution at 50 nm above the surface at SPR resonance of 1015 nm for the case of five minutes electrolysis, and d) the extinction cross section of this assembly of nanocubes as a function of wavelength. In both cases the substrate is copper.

5. CONCLUSION

In conclusion, in this work we prepared a semi-colloidal SERS active substrate by utilizing the electrolysis effect on the copper anode surface. The produced copper oxide nanoparticles on the anode surface in matter of minutes acted as an active medium for SERS. Rhodamine B of concentration of 5 µM used as the electrolyte and its Raman signal at different electrolysis time recorded to obtain the maximum EF. In the carried out experiments we measured more than five orders of magnitude enhancement on the Raman peak of 1509 cm\(^{-1}\) for 90 seconds electrolysis. The EF started to reduce gradually for further electrolysis which after 10 minutes, this value decreased to almost 50 percent of the maximum value. The proposed method has some key advantages: it is a very simple and low cost technique and also can be used in real time since it is a quite fast process.
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