Synthesizing of the SERS-active substrates

E P Kozhina¹, S A Bedin¹, I V Razumovskaya¹ and A V Zalygin¹,²

¹ Moscow State Pedagogical University, Moscow, Russia
² Shemyakin-Ovchinnikov Institute of Bioorganic Chemistry, RAS, Moscow, Russia

E-mail: Liza.kozhina.99@mail.ru

Abstract. We investigated the presence of plasmon resonances (PRs) for substrates with the metallic nanowires (NWs) that were obtained by the matrix (template) synthesis method in the pores of the track membranes. We found experimentally that the location and width of the PRs depend on the diameter of the NWs and on the distance between them. The presence of PRs indicates the potential applicability of such substrates as SERS-active substrates.

1. Introduction

Modern technologies often require the instruments for sensing on single molecule (SM) level. It can be realized by detection of fluorescence [1] or Raman scattering [2] signal. Latter has a principal advantage of SM fingerprint chemical analysis, but it is very complicated for experimental realization in usual condition due to extreme weak signal in comparison with fluorescence. This obstacle was avoided by using the plasmon assisted enhancement of Raman scattering [3]. As an experiment shown, it is possible to achieve the enhancement factor in order of $10^{14-15}$, comparing with usual Raman signal. With the interest in nanoscale devices, there is an increased demand in materials that are able to create EM field enhancement with potential application in sensing. Indeed, such materials can be used as a substrate to give rise to surface-enhancement Raman scattering (SERS).

There are two key mechanisms to enhance the useful signal. The first mechanism is associated with the chemical interaction of the test substance with the surface, which contributes to the enhancement of a signal of the order of $\sim 10^2-10^3$ [4]. The second one is the electrodynamic mechanism, the main idea of which is connected with a collective oscillations of electron (plasmons) that exists at a metal-dielectric interface, where the EM wave propagates at the interface, that is why such type of plasmons called “running plasmons” and we can talk about surface plasmons resonances (SPR). Choosing substrate with a certain degree of roughness, we will get more increased SERS. Going further, we may improve substrate by adding the array of nanowires (NW) on it. It is interesting, because the so-called localized surface plasmon resonances (LSPR) occurs, that is a particular type of SPR, where the EM field remains localized in a nanoscale region around the nanoparticle-dielectric interface. Combining these two types of resonances and changing the interwires spacing we may observe that this leads to the changing of resonance maximum. Note also the local field effect that also can be a reason of strong change of emitting and scattering properties [5].

In case of SERS-active substrates it is appropriate to choose Cu, Ag or Au as a substrate material due to a high concentration of free electrons, choosing one depending on the studying structure, as
each material of the substrate gives resonances in their own regions. Copper nanowires (NWs) can be used to obtain SERS signals in the visible and near infrared range by interaction between the electromagnetic wave incident on the interface between the metal and the dielectric, and free electrons on the sample surface, which are known as surface plasmons, resulting in a resonant interaction. In other words, the electrons begin to oscillate in time with the electromagnetic field oscillations above the metal.

The distance at which the amplitude of the field decreases by a factor of $e$ compared with its initial level is called the penetration depth or skin depth. In the case of very small objects with moving electron clouds, the amplitude of the electric field is large: it is not limited only to the surface of the sample, but propagates in the bulk of the material to a depth

$$d = \frac{1}{a_i} = \frac{2}{\omega(\mu \sigma)\sigma_i^*},$$

where $\alpha$ is the damping constant [3]. For a plane wave in copper at a frequency $10^8$ Hz, $d \approx 770$ nm, at lower frequencies the penetration depth will increase. Since the wire diameter is less than 200 nm, plasmons are excited in the whole volume, which leads to the appearance of a localized surface plasmon (LSPR) [4]. LSPR gives an advantage, as it causes an increase in the intensity of the field in a narrow region.

2. Experimental

In this work, metallic NWs were obtained by the matrix (template) synthesis method in the pores of the track membranes. Polymer films with a thickness of 12 $\mu$m and a pore diameter of 70 and 200 nm and a surface density of $4 \times 10^8$ and $1.2 \times 10^8$ cm$^{-2}$, respectively, were used as the starting material. Previous to, one of the sides of the sample were covered by copper by spaying in order to obtain the conductive layer. The next step was to fill the pores of the membranes by the copper by the electrochemical deposition. To do that membrane with one side covered by copper was put down in the electrochemical cell as a cathode. As the electrolyte was used copper plating electrolyte of the following composition: $CuSO_4 \cdot 7H_2O - 200 g/l, H_2SO_4 - 10 g/l$, the temperature of deposition was $20 - 25^\circ$C. The deposition was carried out at a constant voltage, which made it possible to control the degree of filling of the pores with the metal according to the amount of current flowing through the sample [6, 7]. At the end of the electrochemical deposition, the polymer matrix was removed by dissolving in a concentrated alkali solution (25% NaOH) (figure 1 (a)).

Further, reflection spectra were obtained on the resulting copper substrates with copper NWs. To do that, we used the spectrophotometer SF-2000, which was calibrated on an aluminum mirror. The light of a source in a mirror installation was directed by a mirror at an angle of 45$^\circ$ to the surface of the sample and reflected in the spectrophotometer monochromator, passing through a fiber optic cable housed in a cell compartment. The angle of incidence is selected for reasons of polarization of the material. For successful detection of a LSPR, the light must be polarized, with the following polarization: the electric vector of the electromagnetic wave should lie in the plane of incidence, and the magnetic vector should be parallel to the metal surface [8, 9].

When these conditions are fulfilled, a significant part of the light energy is converted into plasmon energy, due to which the intensity of the light flux reflected from the surface of the metal substrates drops sharply. If the metal film is sufficiently thin (<200 nm), then a significant part of the electromagnetic wave damped in the metal reaches the opposite surface of the metal. The position of the minimum of the localized surface plasmon resonance (LSPR) curve depends on the electric polarization of this medium, in particular, on its dielectric constant (which in the dielectrics equal to the square of the refractive index of light) [3]. In addition, the position of the minimum of the curve depends on the diameter of the NWs, moving to the IR range with increasing diameter of the NWs [3].

3. Results and Discussion

As a test sample, a smooth copper substrate was used (figure 1 (b)), the reflection intensity of which reached 35%, and the frequency of the plasmon resonance was at a wavelength range of 730-760 nm.
We obtained the spectra of the dependence of the reflection coefficient (with the angle of incidence equal to 45°) on the wavelength for NWs with a diameter of 200 and 70 nm, (figure 1 (c, d)). In the spectra, we observe the position of the resonance frequency, located immediately after the reflection peak.

![Figure 1](image)

**Figure 1.** (a) Electron microscopy image of copper substrate with copper NWs on it. Reflection spectra for copper film (b), and for the investigated SERS substrates with the NWs with diameter of 200 nm (c), 70 nm (d).

At the LSPR, the bulk EM wave concentrates on the top of the NW. Like any resonant system, the top of the NW with plasmon resonance accumulates the energy of an EM wave. This is due to the local amplification of the field of an electromagnetic wave at the plasmon resonance near the peak of the NW [10].

In the visible region of the spectrum, along with intraband absorption of light by free electrons, the optical characteristics of metals are affected by interband absorption, which is not described by the Drude – Zener theory. The absorption coefficient increases to 0.2-0.5. In the UV region at $\omega \sim \omega_p$ for all metals, a transition from strong reflection to transparency is typical, due to a change in the nature of the medium’s polarizability and sign $\varepsilon'$. At $\omega \gg \omega_p$ the response of metals to electromagnetic effects is associated with the excitation of radiation of the inner electron shells of atoms and is similar to the response of dielectrics [4].

A contribution to the reflection spectra is made by the distance between the NWs. The distance between NWs with a diameter of 200 nm is of 300 nm, and for NWs with a diameter of 70 nm it is of 110 nm. For the spectrum of NWs with a diameter of 70 nm, the signal-to-noise ratio is better, since with a smaller distance between the NWs, the fields are layered on each other, which results in a
smoother spectrum and there is one main pick of PR. And for the NWs with the diameter of 200 there is bigger amount of PRs, associated with each separate NW. For NWs with a diameter of 200 nm, the area of an electromagnetic wave hit is larger than for NWs with a diameter of 70 nm, which leads to a greater percentage of reflection. The intensity of the peak and half width of the plasmon absorption of real nanosystems depend on the inhomogeneity of the nanoparticles, that is, on the presence of a large number of free electrons. Further, determining the position of the plasmon resonance frequency from the reflection spectra, it is possible to select the source of the corresponding exciting radiation to obtain the resonant SERS.

**Conclusion**
Copper nanowires with a diameter of 70 and 200 nm on a copper metal substrate were synthesized. The reflection spectra of the substrates with NWs were obtained, and its resonance frequency was studied. For samples with a NW diameter of 70 nm, the resonance was found at $\lambda=565$ nm and for NWs with a diameter of 200 nm it is not possible to determine exact wavelength and a resonance is at a region where $\lambda$ varies from 500 to 700 nm.

**Acknowledgment**
We acknowledge with V.V. Artyomov (Shubnikov Institute for Crystallography, Federal Scientific Research Centre “Crystallography and Photonics”, RAS) for his help in obtaining electron microscopic scans. The work was supported by the Ministry of Science and Higher Education and of the Russian Federation (project 3.7990.2017/8.9).

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