

Effect of measurement times in SERS analysis using nanoparticle suspensions and nanostructured surfaces.

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Introduction

Surface enhanced Raman scattering (SERS) is an effect widely used to improve Raman signal allowing detection of analytes under very low concentrations. A great amount of effort has been invested to develop efficient SERS-active substrates, especially of gold and silver¹. Both, nanoparticle suspensions and nanostructured surfaces (which produce high intensity spectra and reproducible response) are desirable for chemical analysis. However, researchers usually do not focus on the response of the substrate for different measurement times. In this work the SERS response as a function of the time for a new nanostructured surface was evaluated and compared to a colloidal gold nanoparticle (AuNP) suspension.

Results and Discussion

Gold-covered Indium tin oxide (ITO) nanowires were grown on 3 mm glass squares by the RF sputtering method. AuNP suspensions were obtained by the Lee-Miesel method². In order to study the response of crystal violet (CV) aqueous solutions as a function of time, the sample was immersed in a 0.1mM solution and the SERS spectra were obtained sequentially with an integration time of 36 s during 1h (PerkinElmer Raman Station 400 F with a 785 nm laser source). AuNPs suspension was mixed to CV solution to obtain a final concentration of 0.1 μ M and the spectra were obtained as cited earlier. The peak height at 1171 cm^{-1} of the CV spectrum was used for the plots. Different concentration values were adopted because there is no overlap between the working ranges of the two types of substrate.

Figure 1 shows the behavior of the peak height as a function of time for the AuNPs and the nanostructured surface. In both cases it was expected a plateau behavior of the peak height after a period of increasing signal dependent on the adsorption time. The plateau can be observed for the AuNPs after about 25 min. In the case of the surface with nanowires no plateau is observed in the time interval studied. The morphology of the surface (see inset in Fig. 1b) made the sample highly hydrophobic and apparently, the analyte takes a long time to penetrate the nanowires and one hour is not enough to reach the equilibrium state. In order to verify the

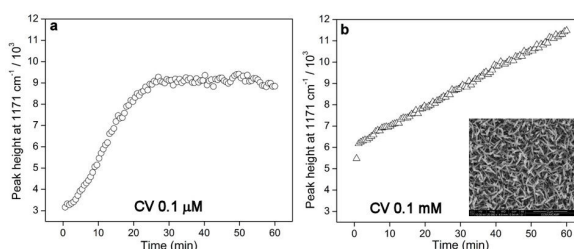


Figure 1. Peak height at 1171 cm^{-1} as function of time obtained with (a) AuNPs and (b) nanowires. Inset shows morphology of the sample.

possibility of using these substrates for chemical analysis in a time shorter than 1h, statistical data were calculated for peak height obtained during two time intervals, 0 to 5 min and 5 to 10 min (Table 1). The results show that for the nanowire surface the relative standard deviation (RSD) was less than 5% in the 5 to 10 min interval, suggesting a possible application of this substrate for chemical analysis. However, the AuNPs exhibited a RSD higher than 7% for both time intervals.

Table 1. Statistical values calculated from results obtained with AuNPs and the gold-covered nanowire surface in two time intervals.

Time interval (min)	Substrate			
	AuNPs		Nanowires	
Peak height Average	3463	4565	6209	6868
SD*	249.0	411.6	331.3	136.6
RSD (%)**	7.19	9.02	5.34	1.99

*Standard Deviation **Relative Standard Deviation

Conclusions

The results show that the time between the moment the analyte is placed in contact with the substrate and the Raman measurement is an important factor, strongly affecting the results.

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² Lee, P.C.; Miesel, D. *J. Phys. Chem.* **1982**, 86, 3391.