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OPTICAL PROPERTIES OF GOLD NANOSTRUCTURES: APPLICATION TO THE SURFACE ENHANCED RAMAN SCATTERING AND TO THE DEVELOPMENT OF A NANOBIOSENSOR

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(Invited paper)

ABSTRACT. The application of Surface Enhanced Raman Spectroscopy (SERS) for detection of biomolecules is a subject of intense current research worldwide. In this article the observation of the dependence of the Raman enhancement versus the nanoparticle size is clearly demonstrated on nanocylinders and nanowires. Remarkably the enhancement is observed to be maximum for a specific diameter or length. We finally show that the SERS signal depends on the molecule used and that the SERS active substrates should be actually optimized for each targeted protein.

1. Introduction

Huge enhancement factors in SERS process can be obtained using substrates such as metallic colloids[1, 2] or metallic island films[3]. These samples are good candidates for single molecule detection[1, 4] but, due to their intrinsic complexity, they are suitable to reach a precise control of their optical properties. Considering only the electromagnetic contribution of SERS and then have a better understanding of the underlying processes, it is important to be able to investigate more "controllable" samples, namely arrays of gold nanoparticles, which can be designed through electron beam lithography and lift off techniques[5, 6, 7]. Thus, we have studied the effect of the size and geometry of nanostructure on their optical properties (localised surface plasmon resonance, LSPR) and their SERS efficiency. For such studies, we have used shape controlled metallic nanocylinders and nanowires which can act as nano-antenna.

2. Results and discussion

The nanocylinder diameters vary from 100nm up to 600 nm whereas the nanowire lengths vary from 50 nm up to 1 m (the width and the height of the nanowires is fixed). The deposited molecular probe used is the trans-1,2-Bis(4-pyridyl)ethylene (BPE) with several excitation wavelengths of 632.8 nm, 676 nm and 785 nm. The observation of the dependence of the Raman enhancement versus the nanoparticle size is clearly demonstrated and



Figure 1. Evolution of the SERS signal depending on length of gold nanowire for two different widths (60 and 70 nm). Probe molecule: BPE, excitation wavelength: 633 nm.

remarkably the enhancement is observed to be maximum for a specific diameter or length (Figure 1).

Moreover, the SERS results can be compared to the particle LSPR and one can determine the specific behaviour of the nanocylinders and nanowires. We notably demonstrate that the best Raman enhancement occurred for a LSPR located between the excitation and Raman wavelengths for nanocylinder whereas, nanowires exhibit the strongest SERS signal for a LSPR position close to the Raman wavelength. For such arrays, we also observe the existence of multipolar surface plasmon modes (up to 7th order) and we show clearly that multipolar LSP modes exhibits a stronger efficiency than the first dipolar order in SERS process[7].

Our results support the fact that the optimization of SERS efficiency, relative to the LSPR, strongly depends on the shape of the metallic nanoparticles. The enhancement strongly depends on the nanoparticle parameters which is a crucial point to determine the optical efficiencies of such structure and to optimise the SERS processes. The nanowire behaviour is also clearly different from the classical behaviour in SERS exhibited by the nanocylinder and it is an actual demonstration that nanowire acts as one nanoantenna at the nanometre scale.



Figure 2. Evolution of the SERS signal depending on the the surface plasmon resonance position of nanocylinders. Probe molecule: Ribonuclease, excitation wavelength: 633 nm.

3. Conclusions

The SERS technique can be used to observe and detect specific molecules such as hydrocarbons or proteins. We demonstrate that the SERS signal depends on the molecule used and that the SERS active substrate should be actually optimised for each targeted proteins (Figure 2). Thus, the detection of molecules with SERS substrate could be used to the design of a new type of nanosensor[8].

Acknowledgments

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