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SURFACE ENHANCED RAMAN SPECTROSCOPY OF BIOMOLECULES IN BUFFER SOLUTION

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ABSTRACT. Controlled creation of SERS-active *hot spots* in liquid is a challenge in which optical forces can play an important role by promoting the aggregation of metal nanoparticles by optical trapping or by exploiting the radiation pressure. Here we show that laser induced aggregation of gold nanorods in a buffered solution of Bovine Serum Albumin (BSA) leads to the formation of SERS-active agglomerates capable to enhance the Raman scattering of BSA by 5 orders of magnitude, thus allowing the detection of BSA at concentrations as low as 10^{-6} M. This occurrence involves optical, mechanical and thermal effects.

1. Introduction

In the last decade, Surface Enhanced Raman Scattering has shown a huge potential for label-free chemical detection down to the single molecule level [1, 2] due to the high field enhancement experienced in particular spatial regions located in the cavities between metal nanostructures aggregates, named "*hot spots*". SERS from aggregates is usually much stronger compared to what is observed on isolated metal nanoparticles, due to the large number of gap regions formed between the adjacent nanoobjects [3].

This phenomenon opens the doors to an interesting application of nanoparticles aggregates as high sensitivity SERS optical biosensors. In particular, the controlled creation of high field enhancement regions in liquid, the natural habitat of biomolecules, is a challenge in which optical forces play an important role by promoting either the trapping of metal nanoparticles in the focus of a laser beam (optical tweezers) [4, 5, 6] or their aggregation on a surface taking advantage of the radiation pressure [7].

Here we report on the implementation of a SERS biosensor based on photothermal aggregation of colloidal gold nanorods in a Phosphate Buffer Solution (PBS) of Bovine Serum Albumin (BSA).

2. Results and discussion

The optical forces and the thermal effects involved during the laser irradiation, promote the formation of aggregates by pushing the nanorods to the bottom of the liquid chamber (Figure 1) where they stick together and mix with the BSA.

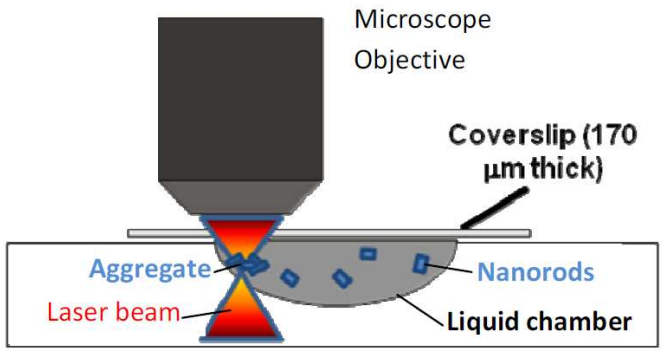

Figure 1. Schematic of the setup showing the nanorods aggregation under the laser beam.

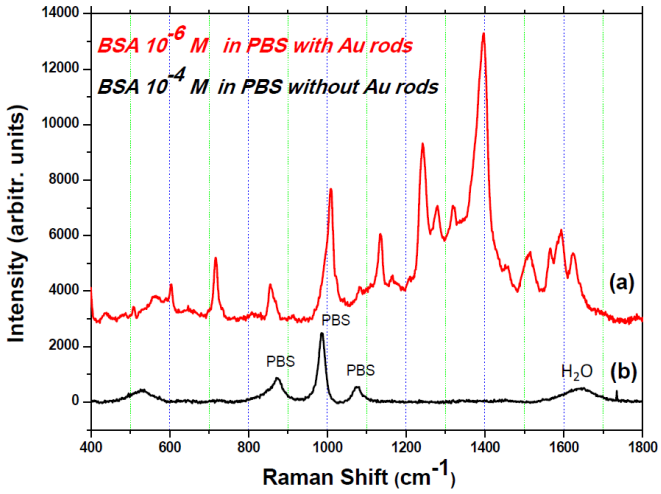

Figure 2. (Red line) SERS spectrum of buffered BSA molecules at 1 mM taken after the formation of the nanorods aggregates. (Black line) Raman spectrum of buffered BSA solution at 100mM without the addition of nanorods. The spectra are offset for clarity.

This occurrence enables the SERS detection of the BSA dissolved at 1mM concentration in a buffer solution (Figure 2, red line), whereas without the rods addition we only detect the PBS and water bands for BSA concentrations up to 100mM (Figure 2, black line). We estimate an enhancement factor of $10^5$by comparing the SERS signal of the phenylalanine ring breathing at 1004 cm^{-1} in presence of nanorods aggregates to the same peak coming from the Raman signal of a buffered solution of BSA 10^{-3} M (corresponding to the detection limit in liquid) without gold nanorods addition.

This in situ methodology has been successfully validated for the Raman detection of others biomolecules in their natural habitat as the phenylalanine amino acid and as the Manganese Superoxide Dismutase (MnSOD) protein [8]. The latter is of particular interest in medical field due to the link between its activity and the level of some severe chronic liver diseases.

3. Conclusions

In conclusion, we report on the implementation of a SERS sensor with photothermally aggregated gold nanorods in liquid environment. This in situ device enables the Raman detection of Bovine Serum Albumin (BSA) molecules dissolved in a Phosphate Buffer Solution (PBS) at 10^{-6} M, compared with a detection limit of conventional microRaman of 10^{-3}M. The methodology and the experimental conditions thus allow for highly sensitive vibrational spectroscopy analysis of biomolecules in their natural habitat.

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