Strathprints Institutional Repository

Graham, Duncan (2010) *The next generation of advanced spectroscopy : surface enhanced raman scattering from metal nanoparticles.* Agewandte Chemie-International Edition, 49 (49). pp. 9325-9327. ISSN 1433-7851

Nanoparticle SERS

DOI: 10.1002/anie.200((will be filled in by the editorial staff))

Surface Enhanced Raman Scattering from Metal Nanoparticles as the Next Generation of Advanced Spectroscopy**

*Duncan Graham**

Nanoparticles; surface enhanced Raman scattering; spectroscopy; sensing

Surface enhanced Raman scattering (SERS) has enjoyed an ever growing research base since its discovery with the number of papers published using the technique and investigating the basis behind it growing exponentially year by year.[1] SERS is an advancement of Raman scattering which overcomes some of the limitations of normal Raman scattering. Raman scattering is a vibrational spectroscopy which gives molecularly specific information relating to specific molecular species. The disadvantage of Raman scattering is that it is an inherently weak process, however it can be used in aqueous solutions, due to water being a weak Raman scatterer, lending itself to analysis and study of molecules in aqueous solution including the study of biomolecules. Another major disadvantage is the fluorescence which often accompanies Raman scattering and can sometimes overwhelm the bands in the spectrum rendering the experiment useless. To overcome this, the phenomenon of surface enhanced Raman scattering can be used.

SERS requires a metal surface, normally of gold or silver, to enhance the Raman scattering through two different mechanisms.[2] The chemical enhancement is viewed differently by physicists and chemists however it involves the interaction of the molecule with the surface of the enhancing metal to form a new charge transfer state, which increases the Raman scattering intensity. The second mechanism is that of electromagnetic enhancement which involves the interaction of the plasmon band of the metal nanoparticle with the molecule to enhance the Raman scattering. Enhancements of up to 10^{14} over normal Raman scattering have been reported[3] and single molecules can be reliably detected with excellent molecular specificity.[4] The two major advantages of using SERS as a technique for either studying molecules vibrationally or as an analytical technique is its exquisite sensitivity coupled with its molecular specificity. Mixtures of components can be identified without separation making the technique more amenable to more complex analysis than the equally sensitive fluorescence spectroscopy.[5] Essentially to achieve SERS, the molecule of interest must be adsorbed onto a suitable roughened metal surface. The format of the metal surface has traditionally been either electrodes, vapour deposited films or more commonly nanoparticles.[6] All of these types of surfaces have issues in terms of specific surface adsorption of the analyte and the ability to be ubiquitous surfaces to provide enhancement of difficult to adsorb species which means that one surface tends not to work for all SERS experiments.

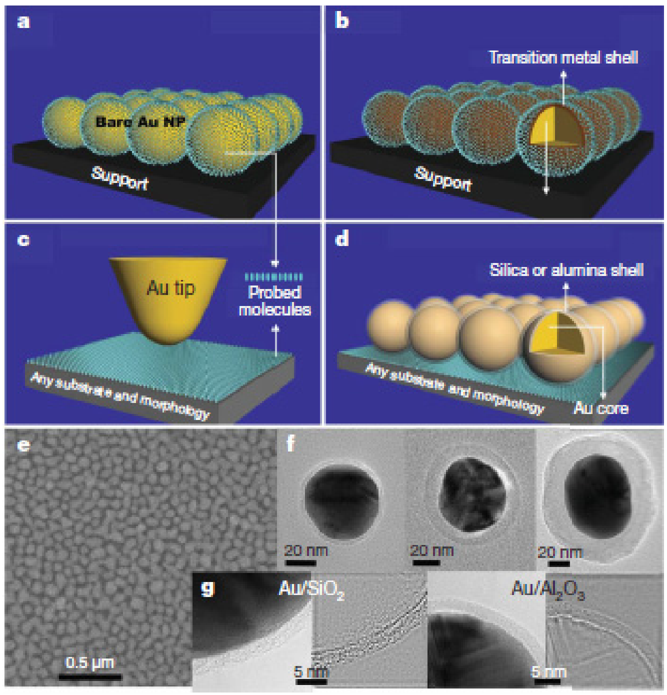


Figure 1*.* The working principles of SHINERS compared to other modes. Schematic of the contact mode. a, Bare Au nanoparticles: contact mode. b, Au core–transition metal shell nanoparticles adsorbed by probed molecules: contact mode. c, Tip-enhanced Raman spectroscopy: noncontact mode. d, SHINERS: shell-isolated mode. e, Scanning electron microscope image of a monolayer of Au/SiO2 nanoparticles on a smooth Au surface. f, HRTEM images of Au/SiO2 core–shell nanoparticles with different shell thicknesses. g, HRTEM images of Au/SiO2 nanoparticle and Au/Al2O3 nanoparticle with a continuous and completely packed shell about 2nm thick.[8]

[*] Prof D Graham
Centre for Molecular Nanometrology
WestCHEM, Pure and Applied Chemistry
University of Strathclyde
Glasgow
G1 1XL, UK

E-mail: duncan.graham@strath.ac.uk
Homepage ((optional)):
http://www.chem.strath.ac.uk/people/academic/duncan_graham

Recently there has been a large increase in the investigation and use of metal nanoparticles shelled with a protective coating which can be used in a number of ingenious methods.[7] Many coatings have been examined, however for the purposes of this article only a silicon coating will be focused on. In a very elegant approach Tian and co workers have developed a *shell isolated nanoparticle enhanced Raman spectroscopy* based system known as SHINERS.[8] In this approach, gold nanoparticles are shelled in a very thin silica or alumina shell which is typically less than 2 nm thick. (Figure 1) These particles can then be deposited onto either a surface to provide a monolayer of nanoparticles to act as an enhancing surface or deposited onto a target of interest such as a cell. The silica or alumina coat acts as a protective coating to avoid unwanted interaction with the gold from non specific species, however it also allows adsorption of the target analyte to be close enough to the gold to experience electromagnetic enhancement and hence an increase in the Raman scattering.

The authors demonstrate the applicability of this approach through the detection of the adsorption of hydrogen onto single crystal platinum surfaces which cannot be measured by conventional vibrational spectroscopy. In a further example of the power of the SHINERS, a single yeast cell was exposed to the gold-silica nanoparticles and Raman spectra accumulated across the cells. In comparison to normal Raman spectra of these yeast cells, there were enhancements of bands corresponding to protein backbones and amino acids. This demonstrates the potential for the examination of living cells at a biomolecular level in an information rich manner. In a final advancement of the application of SERS in situations which are often difficult to achieve, the SHINERS were applied to the surface analysis of citrus fruits. The hypothesis tested was to examine whether surface deposition of pesticide residues, such as parathion, can be detected on the citrus fruits. When the SHINERS were applied to a fresh orange and examined using a portable Raman spectrometer, spectra which were clearly identified as coming from the parathion, were identified whereas control experiments where normal Raman scattering was used, failed to produce confirmation of the presence of the pesticide. Taken together, these three examples indicate the versatility and applicability of these new self contained Raman enhancing surfaces and also their ease of application in a range of situations which cannot be examined by conventional Raman spectroscopy.

An alternative to using the metal nanoparticles as a purely enhancing surface for target species is to use a metal nanoparticle as a SERS label. In this case, nanoparticles are functionalised with a Raman reporter molecule which gives a strong characteristic Raman spectrum from the species adsorbed onto the surface of the metal nanoparticle. This can then be encapsulated in a silica shell locking the SERS signal on permanently and protecting the nanoparticle from the interrogation environment.[7b] A number of groups have been working on this approach to provide SERS active nanoparticles capable of being used for bioanalysis and Schlücker and co workers have recently reported the synthesis of SERS labels for NIR laser excitation.[9] In this approach the authors used a self assembled monolayer on a single colloidal gold-silver nano shell which has a tuneable plasmon resonance moving towards the near infrared region of the electromagnetic spectrum. The shell can then be functionalised with a biomolecular probe. (Figure 2) This is important for biological analysis as it minimises cellular or tissue auto fluorescence which can dramatically affect the signal to background ratio and allows analysis in the spectroscopic biological window.

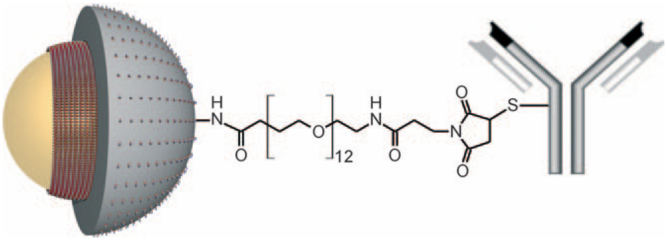


Figure 2. Structure of silica-encapsulated and biofunctionalized SERS labels. Left: Gold/silver nanoparticle with a SAM of Raman label molecules (red) and a protective silica shell with amino groups (gray). Middle: heterobifunctional polyethylene glycol spacer. Right: monoclonal antibody for antigen recognition. 9

A gold nanoparticle was shelled with silver and a self assembled monolayer of the Raman label, (mercaptonitrobenzoic acid) was then coated by layer by layer deposition with polyelectrolytes followed by silica shelling by a modified Stöber method. The surface of the silica was then functionalised with an antibody that recognises prostate specific antigen (PSA) and the SERS active nanotags were used to image PSA in a tissue sample. In a more recent advance of this approach the group have synthesised a silane functionalised reporter molecule which self assembles on the nanoparticle surface and can then be cross linked through the addition of tetraethyl orthosilicate (TEOS) to form a silica encapsulated nanoparticle with a well controlled ratio of reporter to nanoparticle.[10] This is an important step forward in the synthesis of tuneable SERS labels which can subsequently be functionalised to provide unique vibrational codes for a number of different target species. In this case the approach was exemplified using an antibody targeting its antigen in a tissue sample, however there are many alternatives which can be used based on this initial work.

In summary, the field of SERS has generated some very noteworthy advances in recent years which have provided new approaches to surfaces for the enhancement, but also harnessing the enhancement capability to act as labels for target species. These examples provide great confidence that the field is growing in terms of innovation and acceptability through the wider scientific community and looks set to continue its dramatic advancement over the coming years.

Received: ((will be filled in by the editorial staff))
Published online on ((will be filled in by the editorial staff))

[1] D. Graham, R. Goodacre, *Chem. Soc. Rev.* **2008**, *37*, 883.
[2] M. Moskovits, *Rev. Mod. Phys.* **1985**, *57*, 783.
[3] X. M. Qian, S. M. Nie, *Chem. Soc. Rev.* **2008**, *37*, 912.
[4] a)J. A. Dieringer, R. B. Lettan, K. A. Scheidt, R. P. Van Duyne, *J. Am. Chem. Soc.* **2007**, *129*, 16249; b)E. C. Le Ru, M. Meyer, P. G. Etchegoin, *J. Phys. Chem. B* **2006**, *110*, 1944.
[5] a)K. Faulds, R. Jarvis, W. E. Smith, D. Graham, R. Goodacre, *Analyst* **2008**, *133*, 1505; b)K. Faulds, F. McKenzie, W. E. Smith, D. Graham, *Angew. Chem. Int. Ed.* **2007**, *46*, 1829.
[6] A. Campion, P. Kambhampati, *Chem. Soc. Rev.* **1998**, *27*, 241.
[7] a)L. M. LizMarzan, M. Giersig, P. Mulvaney, *Langmuir* **1996**, *12*, 4329; b)S. P. Mulvaney, M. D. Musick, C. D. Keating, M. J. Natan, *Langmuir* **2003**, *19*, 4784.
[8] J. F. Li, Y. F. Huang, Y. Ding, Z. L. Yang, S. B. Li, X. S. Zhou, F. R. Fan, W. Zhang, Z. Y. Zhou, D. Y. Wu, B. Ren, Z. L. Wang, Z. Q. Tian, *Nature* **2010**, *464*, 392.
[9] B. Küstner, M. Gellner, M. Schütz, F. Schöppler, A. Marx, P. Ströbel, P. Adam, C. Schmuck, S. Schlücker, *Angew. Chem. Int. Ed.* **2009**, *48*, 1950.
[10] M. Schütz, B. Küstner, M. Bauer, C. Schmuck, S. Schlücker, *Small* **2010**, *6*, 733.

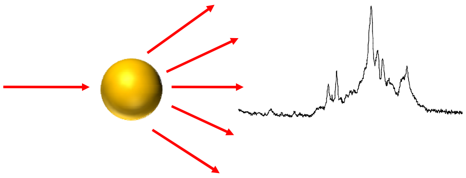
Entry for the Table of Contents

Nanoparticle SERS

Duncan Graham*

_________ **Page – Page**

Surface Enhanced Raman Scattering from Metal Nanoparticles as the Next Generation of Advanced Spectroscopy



SERS is a technique which offers much in terms of molecularly specific information and at ultra sensitive levels. This highlight focuses on two recent aspects of breakthroughs in SERS. In the first example a new surface is described that allows SERS to be obtained from situations previously impossible and the second a nanoparticle SERS label is used to image antigen relating to cancer in tissue.