Chemical and bioanalytical applications of surface enhanced Raman scattering spectroscopy

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Raman spectroscopy is a highly versatile physicochemical technique that provides vibrational fingerprints from chemical and biological materials. The Raman spectrum that arises from the interrogation of chemical species can be readily interpreted and used to identify specific chemical species in mixtures and to quantify their levels accurately. However, the non-resonance Raman effect is very weak and typically only 1 in 10^{6-8} photons undergo an inelastic light scattering event. This inherent lack of sensitivity has restricted the use of this potentially very powerful technique in areas where sensitivity is an issue.

In 1974 Fleischmann and colleagues[1a] reported the Raman spectra from pyridine adsorbed onto a roughened silver electrode which was the first peer reviewed mention of this phenomenon although a previous disclosure at a Faraday discussion[1b] had prepared those in the field for this observation. This caused great excitement and others soon discovered that Ag and Au sols as well as thin films of these metals also gave remarkable enhancements; thus the method of 'surface enhanced Raman scattering' was conceived. Interest in this new method grew exponentially and is still growing today as is evident from Fig. 1, with ~1000 papers published annually either studying or using the technique. Also shown in this figure are some of the more significant events in the development of SERS, and it is perhaps unsurprising that reports of enhancement factors of 10^{14} and single molecule detection has resulted in flurries of activities.

"*There is an epoch in the growth of a science during which facts accumulate faster than theories can accommodate them.*"

P. Medawar, in *Pluto's Republic*, OUP, Oxford, 1982, p. 29.

The above quote is rather apt for SERS since the exact theory of how the SERS effect occurs has not yet been fully elucidated. Rather than temper the enthusiasm for this technique, chemists in diverse fields are continuing with great gusto to study SERS and the related SERRS (an additional resonance effect occurs from an absorbing chromophore). It is therefore the application of these methods for chemical and bioanalytical applications that is the subject matter for this special issue.

Nevertheless it is of course important to consider the various mechanisms involved in SERS and Tian provides an introduction to early work on SERS and then covers the continuation of electrochemical SERS since the original reports on silver electrodes. The emergence of the importance of the resonance contribution with the surface enhancement is discussed by Smith and guidance given on how practically to choose experimental setups to suit the system under study. In order to perform these methods in a robust way so as to generate reproducible data, various substrates are needed. Mirkin reviews the rational design of nanostructures, and tailoring plasmonic substrates is detailed by Halas. Jensen and Schatz review electronic structure methods that are used for studying SERS, whilst Cohen and co-authors discuss advances in vibrational pumping in SERS experiments.

In addition to the traditional approach of using Raman spectroscopy, alternative measurement techniques for enhanced Raman measurements are being developed and Deckert provides an in-depth overview of tip-enhanced Raman scattering (TERS), and Blanch a discussion of combining SERS with Raman optical activity (SEROA) to gain chiral specific information from biochemical species.

The ability to detect single molecules by SERS was first reported in 1997[4,5] and demonstrates the exquisite sensitivity of the technique. Recent progress in the fundamental mechanisms and application of SERS at the single molecule level is reviewed in articles by Aroca and Kneipp who also discusses surface enhanced hyper Raman scattering (SEHRS).

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Roy Goodacre is Professor of Biological Chemistry at The University of Manchester. The research group's (http://www.biospec.net/) interests are broadly within bioanalytical chemistry, and in the application of a combination of a variety of modern spectroscopies (including Raman, IR and MS) and advanced chemometrics and machine learning to the explanatory analysis of complex biological systems within a metabolomics and proteomics context.

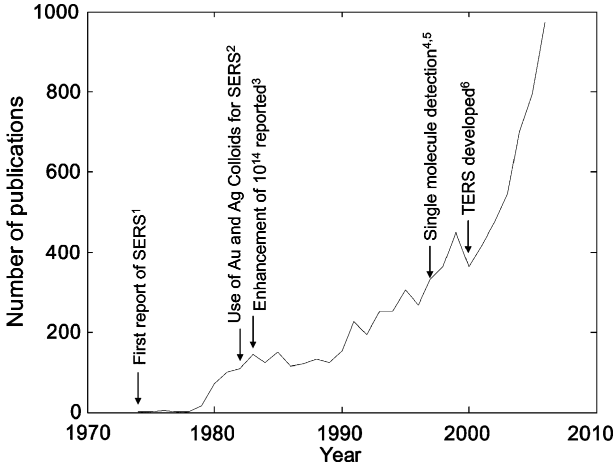

Fig. 1 Results of bibliometric analysis of the number of publications per year listed on ISI Thomson Web of Science1 (http://wos.mimas.ac.uk/), using the search term ((surface enhanced Raman) OR (surface enhanced resonance Raman)). Also highlighted are the most significant advancements in the field.

Raman is obviously a quantitative method and there is every expectation that this is also the case when the method is enhanced. This realisation is reviewed by Bell for SERS and by Graham and Faulds for the analysis of specific DNA sequences using SERRS. SERS as a detection method for bioanalytes is reviewed by Porter who discusses the fundamentals, design, and applications of SERS as a viable bioassay platform, and Nie reviews the use of SERS nanoparticle tags for *in vivo* imaging.

Finally, Jarvis and Goodacre illustrate how SERS can be used for the identification of low numbers of bacteria, Hildebrandt for furthering the understanding of the interfacial redox processes of proteins, and Sockalingum gives an interesting overview of intracellular SERS and the potential this has for single cell imaging.

In summary, this special issue aims to highlight the latest developments and applications of SERS. It contains tutorial and critical reviews that encompass a diverse range of applications. We hope you enjoy them and your thoughts and comments can be emailed to us at our addresses given in this editorial.

References

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