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# Surface-enhanced Raman spectroscopy: advancements and applications

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Since the mid-1990s, surface-enhanced Raman scattering (SERS) has advanced greatly and gained wider application and a renewal of interest. There have been several new and creative developments, e.g. SERS of single molecules, nanostructures and transition metals, tip-enhanced Raman scattering (TERS), surface-enhanced hyper-Raman scattering (SEHRS), ultraviolet-excited SERS (UV-SERS) and surface-enhanced resonance Raman scattering (SERRS), and their wide applications in biology, medicine, materials science and electrochemistry. It is timely to publish a special issue reporting these initiatives and the progress made in the past 7 years. This issue consists of 30 invited articles that are roughly divided into three SERS research themes: theories, methods and applications. These up-to-date representatives of the research results clearly show that SERS is important not only for Raman spectroscopy and surface science but also for nanoscience. Copyright © 2005 John Wiley & Sons, Ltd.

**KEYWORDS:** surface-enhanced Raman scattering; SERS mechanisms; SERS applications; nanostructures; nanoparticles

## INTRODUCTION

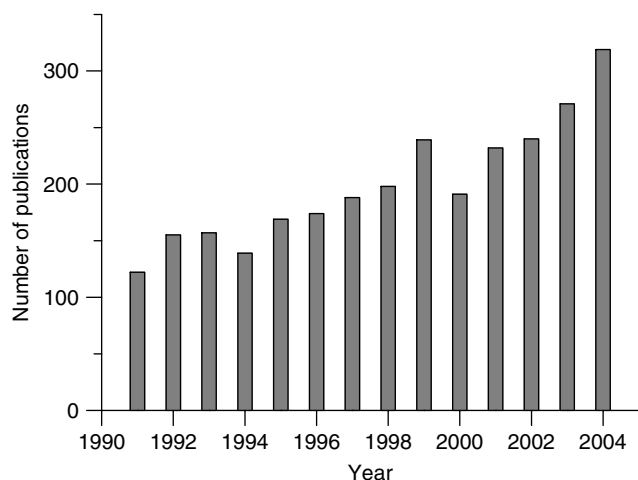
The explosion of activity in the field of surface-enhanced Raman scattering (SERS) started in the mid-1970s. The first measurement of a surface Raman spectrum from pyridine adsorbed on an electrochemically roughened silver electrode was reported by Fleischmann, Hendra and McQuillan in 1974,<sup>1</sup> which stemmed from their pioneer work on the application of Raman spectroscopy to electrochemistry.<sup>2</sup> This was in fact the first SERS measurement, although it was not recognized as such at that time. They initially thought that the intense surface Raman signal of pyridine adsorbed on a silver electrode was due to the electrochemical roughening procedure that significantly increased the electrode surface area. Van Duyne and Jeanmaire very carefully combined experiments and calculations to realize that the major contribution to the intense Raman signal was an enhancement of  $10^5$ – $10^6$  times in the scattering cross-section of the bulk pyridine.<sup>3</sup> After an exhaustive review process, presumably due to the reluctance of referees to believe the unorthodox concept of surface enhancement, their work was eventually published in 1977, and Albrecht and Creighton independently reported a similar result.<sup>4</sup> These pioneering works provided strong evidence demonstrating that the

enormously strong surface Raman signal must be caused by a true enhancement of the Raman scattering efficiency itself. This effect was later called surface-enhanced Raman scattering (SERS).<sup>5</sup>

The discovery of SERS had far-reaching consequences in both fundamental and applied research. It not only provided a stimulus for the study of enhanced optical scattering from interfaces, but also opened up a new field of surface-enhanced spectroscopy that includes surface-enhanced second-harmonic generation (SE-SHG),<sup>6,7</sup> surface-enhanced infrared spectroscopy (SEIRS),<sup>8,9</sup> surface-enhanced fluorescence (SEF)<sup>10,11</sup> and surface-enhanced sum frequency generation (SE-SFG).<sup>12,13</sup> Moreover, it offered an ultrasensitive and *in situ* diagnostic probe for the determination of the detailed structure and orientation of molecules on the surface that is widely applicable to biological, electrochemical, catalytic and other ambient interfaces.<sup>14–17</sup>

Thirty-one years after the first observation and 28 years after the discovery of SERS there have been more than 4000 papers published on the subject, including some excellent review articles<sup>18,19</sup> and a book.<sup>20</sup> In 1998, the *Journal of Raman Spectroscopy* (JRS) published a special issue under the title 'Surface-enhanced Raman spectroscopy: new trends and applications'.<sup>21</sup> Since then there have been some remarkable advancements, including: the development of single-molecule SERS (SM-SERS), surface-enhanced hyper-Raman spectroscopy (SEHRS) and surface-enhanced resonance Raman spectroscopy (SERRS); the initiation of

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**Figure 1.** The number of publications in the 1991–2004 period by a simple search through the ISI Web of Science® using the keywords ‘SERS’ and ‘surface enhanced Raman’.

tip-enhanced Raman spectroscopy (TERS) and ultraviolet-excited SERS (UV-SERS); new progress of SERS from various nanostructures and transition metals; and in biological and medical applications. Indeed, a simple search through the ISI Web of Science® using the keywords ‘SERS’ and ‘surface enhanced Raman’ yields 1104 published papers in the period between 1991 and 1997. The number of publications increased in the 1998–2004 period by more than 50% up to 1690 papers in total (see Fig. 1). It is thus timely and desirable to have another JRS special issue about SERS to report the initiatives and progress in the field in the past 7 years.

This special issue consists of 30 invited articles, including contributions from many leading groups in this area. The first paper is authored by Van Duyne and co-workers.<sup>22</sup> This special arrangement is to honour him as a pioneer in the field and to recognize his significant contributions to the development of SERS for about three decades. His detailed retrospect on the discovery of SERS is valuable for all readers, especially for the SERS community. This paper mainly reviews their recent contributions to the development of a general rule for optimizing the enhancement factor on nanofabricated substrates with narrow localized surface plasmon resonances and the exploitation of these optimized SERS substrates for environmental and biomedical sensing applications.

The other 29 articles are roughly classified into three important SERS research themes: theories, methods and applications. In fact, some articles cover more than one theme with a certain degree of overlap. Indeed, these synergetic efforts have advanced the SERS research to a higher level.

In the first theme, various theoretical approaches at different levels are presented and reviewed. Moskovits gives a brief review recapitulating the broad outline of the electromagnetic theory of SERS, illustrating how it accounts for the most basic observed features of SERS and explaining

that the overall reason why SERS produces such inordinate enhancements is largely due to the electromagnetic property of nanostructures.<sup>23</sup> Otto updates his view on the chemical (electronic) contribution to SERS by giving further experimental evidence for the electronic interaction between metal and adsorbate, especially at SERS-active sites.<sup>24</sup> Käll *et al.* describe a theoretical analysis of surface-enhanced Raman and fluorescence emission from chromophoric molecules located at electromagnetic ‘hot spots’ in nanoparticle aggregates. The model combines classical electrodynamic enhancement effects with molecular quantum dynamics to quantify various molecular cross-sections and spectral properties.<sup>25</sup> Otero and co-workers discuss the photo-induced charge-transfer process between metallic nanostructures and adsorbates and then briefly explain a general methodology to detect this process.<sup>26</sup> Polubotko presents his view on the dipole–quadrupole theory and uses it to explain the SERS spectra of some aromatic molecules adsorbed on transition metals.<sup>27</sup> Wu *et al.* report a hybrid density functional theory study on the binding interaction and Raman spectral properties of pyridine–metal clusters by correlating its surface chemistry and the relative intensity of SERS spectra.<sup>28</sup>

The second theme presents state-of-the-art SERS methodologies that are further divided into two parts: advances in techniques and substrates. Pettinger *et al.* first present a mini-review of TERS as one of the most promising techniques in this field. A scanning probe microscopy tip can be used as the SERS-active substrate to probe adsorbate at any surface, including an atomic smooth single-crystalline surface. They then focus on the study of the TERS intensity decay during bleaching and the distribution of the enhanced electromagnetic field below the tip.<sup>29</sup>

Two articles report important progress in surface-enhanced hyper-Raman spectroscopy (SEHRS) to overcome its weak scattering cross-section and experimental challenges. Kneipp *et al.* studied SEHRS of molecules in silver colloidal solutions under non-resonant and resonant conditions. They also explored the capability of SEHRS for trace detection and demonstrated the detection and identification of crystal violet down to nanomolar concentrations.<sup>30</sup> Li and co-workers developed a substrate named ‘metal nanoparticles-on-smooth-electrode’ that exhibits very high SEHRS activity<sup>31</sup> and they performed systematic experimental and theoretical studies on potential-dependent surface-enhanced hyper-Raman, hyper-Rayleigh and Raman scattering of adsorbed molecules.

Three papers present new approaches in single-molecule SERS (SM-SERS). Aroca and co-workers demonstrate that Raman microscopy combined with the surface-enhanced resonance Raman scattering (SERRS) effect is a uniquely successful technique for mapping single molecules from Langmuir–Blodgett monolayers on nanostructured silver island films.<sup>32</sup> Futamata and Maruyama report critical evidence that individual molecules adsorb at the nanoparticle junction to yield enormous enhancement and blinking. Such

evidence is based on the correlation between SERS activity, elastic scattering, emission spectra and numerical simulation for far-field scattering.<sup>33</sup> Sasic *et al.* report a systematic SERRS study of rhodamine 6G with different concentrations of the dye on silver nanoparticles. The problem of band assignment of single-molecule spectra of biological species is addressed.<sup>34</sup>

Another advance in methodology is the use of different laser excitations. Smith and co-workers compared pulsed and continuous wave lasers as excitation sources for SERRS. The lower peak power high-repetition-rate laser may be a more effective excitation source; the high-powered pulsed lasers do not appear to be very efficient and their limitations are addressed.<sup>35</sup> Ren *et al.* report that SERS can be excited successfully with an ultraviolet laser and the UV-SERS of various adsorbates on different transition-metal electrodes is presented. The surface enhancement factor of a rhodium electrode was estimated to be about two orders of magnitude in the UV region.<sup>36</sup>

The design and fabrication of a variety of nanoparticles and nanostructures as new SERS substrates has been a hot topic in this field since the mid-1990s. Two groups report the successful extension of SERS-active substrate to transition-metal systems. Perez and co-workers obtained high-quality SERS spectra of various species on nanostructured electrodes prepared by the deposition of Pt, Pd, Rh and Pd–Pt nanoparticles on either gold or platinum electrodes. Specific advantages of this ‘nanoparticles-on-electrode’ approach are highlighted.<sup>37</sup> Kim and co-workers studied SERS of benzenethiol adsorbed at platinum nanoparticles and SERRS of rhodamine 6G at those Pt nanoaggregates on Si wafers at 514.5, 568 and 632.8 nm excitation.<sup>38</sup>

Brolo *et al.* introduce a simple way to prepare the SERS-active surface by performing a series of scratches in a 100-nm-thick gold film deposited in glass. The SERS intensity from these substrates is polarization dependent, with a maximum enhanced signal observed when the electric vector of the incident field is perpendicular to the direction of the scratches.<sup>39</sup> Zhao and co-workers report a new method for substrate preparation. The self-assembled technique is explored to prepare high-SERS-active silver nanostructures. The important influences of the stabilizer on size distribution, formation and transfer of metal nanoparticles are discussed in detail.<sup>40</sup>

The third theme covers the application-oriented investigations, which can be divided roughly into three parts: biomedical, materials and electrochemistry. The most exciting and demanding applications are biology and medicine. Vo-Dinh *et al.* present recent developments and applications of SERS for use in medical diagnostics and biological imaging, such as gene detection and cellular imaging. They also describe a hyper-spectral surface-enhanced Raman imaging (HSERI) system with high spatial and temporal resolution.<sup>41</sup> To prevent the structural and functional changes due to interaction of biomolecules with the substrate, Thoreson and

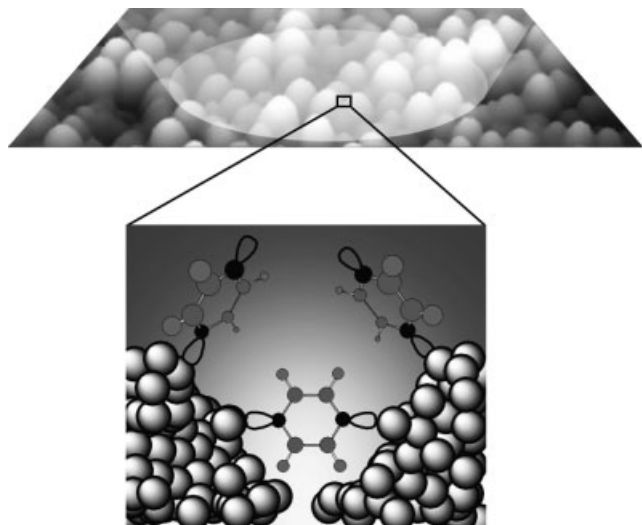
co-workers developed adaptive silver films in which the bio-material and the substrate act in concert to produce excellent Raman enhancement through local restructuring of the metal surface. These films show great promise for SERS of many different types of biomolecules.<sup>42</sup>

Comparative studies of SERS, normal Raman and resonance Raman scattering appear to be very useful in characterizing some more complex bio-related systems. Kiefer and co-workers provide a good example of vibrational characterization of food additives by Raman, SERS and theoretical studies. The spectra recorded at different concentrations can be used as a data bank for further applications in the trace analysis of food products.<sup>43</sup> Zeir and Efrima developed rather robust methods to incorporate silver and gold colloids in bacteria and to measure their SERS spectra using several laser excitations. The SERS spectra obtained are compared with the normal and resonance Raman results.<sup>44</sup>

Surface-enhanced Raman spectroscopy also provides an advantage in the detailed structural characterization of various materials such as carbon nanotubes, polymers and self-assembled layers. Lefrant *et al.* report their systematic SERS study on single-walled carbon nanotubes, with emphasis on chemically transformed carbon nanotube thin films.<sup>45</sup> Xue and co-workers used the entropic depletion effect on a super-molecular assembly of bipyridine and two engineering polymers, and SERS is then used to characterize their ordered structures.<sup>46</sup> Liu and co-workers report a two-step method to obtain the very high SERS activity of polypyrrole electrodeposited on a roughened gold substrate modified with finer silver nanoparticles.<sup>47</sup> Kudelski *et al.* demonstrate the applicability of SERS to determine the conformation and the  $pK_a$  values of thiol molecules consisting of self-assembled monolayers formed on silver and copper surfaces, respectively.<sup>48</sup>

Finally, with regard to the extension of electrochemical applications to more complicated and applied systems, Gewirth and Li report an *in situ* SERS study of hydrogen peroxide electroreduction on a lead-modified gold electrode; the electroreduction mechanism was examined in detail.<sup>49</sup> Cao and Gu describe some advanced studies with the objective of illustrating the virtues of SERS as a versatile tool to examine not only aqueous but also non-aqueous interfaces for transition metals.<sup>50</sup> Chen and Otto report an interesting approach on potential-dependent SERS of water at single-crystalline Cu electrode surfaces, using the resonance of surface plasmon polaritons in an attenuated total reflection configuration; the enhancement by an electronic impact mechanism is proposed.<sup>51</sup>

It has been shown throughout this issue that SERS has greatly advanced and gained wider application since the mid-1990s. The renewal of interest has been promoted significantly by the development of Raman instrumentation and laser technology, and especially by the blooming development of nanoscience. These up-to-date representatives of research results clearly position SERS as an important



**Figure 2.** Schematic illustration of multiple interactions and strong couplings of light-molecule-nanoparticles (-nanostructures).

issue not only for Raman spectroscopy and surface science but also for nanoscience. Indeed, SERS is among the most interesting and complicated subjects in nanoscience. In most cases SERS involves multiple interactions and strong couplings of light-molecule-nanoparticles (see Fig. 2), although there have been good quantitative theories dealing with the interaction of light-molecule, light-nanoparticle or molecule-nanoparticle, respectively. It seems to be essential to enhance further the interdisciplinary collaborative research on SERS and other surface-enhanced spectroscopies by mutual understanding and knowledge exchanging in several related areas of physics, chemistry and spectroscopy. It is also highly desirable to improve the stability and reproducibility of nanostructures and the quantitative level in theory and methods. These synergetic efforts are transforming SERS in a routine technique adopted by broad communities in surface, analytical, materials, life and nano sciences.

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