



Editorial

Special issue on surface-enhanced Raman spectroscopy

Guest editors

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Although Raman scattering spectroscopy was theorized [1] and demonstrated [2] in the late 1920s, its inherent molecular cross-sections, and the lack of appropriate stable sources and optics, hindered its application until the 1960s. During these years the development of resonance Raman [3], which added up to five orders of magnitude intensification to the Raman signal, led to the rebirth of the technique. Following intensified research in the field, in 1974, Fleischmann *et al* discovered, by accident, an anomalous intensification of the Raman signal when studying the interaction of pyridine with a silver electrode [4]. These authors interpreted the effect as a local increase of the surface concentration of the analyte due to the increase of the surface area of the electrode from its deterioration as a consequence of the consecutive reduction–oxidation cycles. Consequently, the physical effect was incorrectly named surface-enhanced Raman scattering (SERS) spectroscopy.

In 1977 two different key manuscripts, by Jeanmaire and Van Duyne [5] and Albrecht and Creighton [6], reported the SERS as a pure electromagnetic effect. In 1980 Otto reported the effect of the charge transfer and the resonance at the surface, the so called chemical effects, on the intensification of the SERS signal [7]. In 1983/84 the surface selection rules were developed independently by Creighton [8] and Moskovits and Suh [9]. Despite these advances, reported by Moskovits in one of the most influential reviews in SERS [10], the research and use of this technique remained mostly confined to academic levels until 1997. During this year two different papers demonstrated the capability of SERS for the detection of single molecules [11, 12]. This fact not only fueled basic research in the field but also in close areas such as nanofabrication, optic theory and the development of applications in biology, medicine, environmental sciences or catalysis. Thus, today an extraordinary effort led by a myriad of research groups is performed to transform SERS into a real live tool, especially in field of biosciences.

This special issue contains 23 papers which envision enlightening the field of SERS from the pure theoretical basics and nanomaterial fabrication to the final development of applications. The issue begins with two reviews summarizing the effects of nanogaps on the SERS intensity of the target probes [13] and the use of SERS encoded particles as contrast agents for optical bioimaging [14]. This collection of papers also contains 21 research articles related to a variety of topics. First, the formal theoretical basis of the effects of multipole surface plasmon resonances on the SERS signal is discussed in a short note [15]. Also, the use of the powerful and well-established static DFT methods for the assignment of the vibrational modes are compared with the state-of-the-art time-dependent DFT approaches [16]. Next, some examples are included for the use of SERS as a characterization tool for plasmonic materials [17, 18] and the effects of the polarized light [19] on the resulting signal. The increase of SERS efficiency by the generation of the plasmonic intercouplings, known as hot spots, [20] and some of their methods of preparation are reported for gold nanoparticle monolayer films [21, 22], gold nanorods [23] or discrete plasmonic microparticles [24]. Regarding the preparation of the plasmonic materials for SERS, here we include examples of

gold nanostars [25], hybrid magnetic plasmonic particles [26], hybrid polymer nanoparticle films [27] and silica coated plasmonic films [28] and particles [29]. Finally, the potential of SERS to solve real life applications is illustrated through monitoring of the molecular dynamics of a chromophore [30]; the ultrasensitive detection of the chemotherapeutic agent paclitaxel [31], glucose [32] or DNA [33] and their modifications [34]; and the 3D intracellular monitoring of the transportation of nanoparticles in the cytosol [35].

In summary, we hope this collection of articles will stimulate innovative new research in this growing field of SERS by showcasing new advances in characterization and fabrication techniques and applications such as the ultrasensitive detection of analytes, monitoring of complex biological systems or the study of the dynamics of molecules.

References

- [1] Smekal A 1923 The quantum theory of dispersion *Naturwissenschaften* **11** 873–5
- [2] Raman C V and Krishnan K S 1928 A new type of secondary radiation *Nature* **121** 501–2
- [3] Albrecht A C 1961 On the theory of Raman intensities *J. Chem. Phys.* **34** 1476–84
- [4] Fleischmann M, Hendra P J and McQuillan A J 1974 Raman spectra of pyridine adsorbed at a silver electrode *Chem. Phys. Lett.* **26** 163–6
- [5] Jeanmaire D L and Van Duyne R P 1977 Surface raman spectroelectrochemistry *J. Electroanal. Chem. Interfacial Electrochem.* **84** 1–20
- [6] Albrecht M G and Creighton J A 1977 Anomalously intense Raman spectra of pyridine at a silver electrode *J. Am. Chem. Soc.* **99** 5215–7
- [7] Billmann J, Kovacs G and Otto A 1980 Enhanced raman effect from cyanide adsorbed on a silver electrode *Surf. Sci. Lett.* **92** A50
- [8] Creighton J 1983 Surface Raman electromagnetic enhancement factors for molecules at the surface of small isolated metal spheres: the determination of adsorbate orientation from SERS relative intensities *Surf. Sci.* **124** 209–19
- [9] Moskovits M and Suh J S 1984 Surface selection rules for surface-enhanced Raman spectroscopy: calculations and application to the surface-enhanced Raman spectrum of phthalazine on silver *J. Phys. Chem.* **88** 5526–30
- [10] Moskovits M 1985 Surface-enhanced spectroscopy *Rev. Mod. Phys.* **57** 783–826
- [11] Kneipp K *et al* 1997 Single molecule detection using surface-enhanced Raman scattering (SERS) *Phys. Rev. Lett.* **78** 1667
- [12] Nie S and Emory S R 1997 Probing single molecules and single nanoparticles by surface-enhanced Raman scattering *Science* **275** 1102–6
- [13] Kiguchi M, Marqués-González S and Matsushita R 2015 Surface enhanced Raman scattering of molecules in metallic nanogaps *J. Opt.* **17** 114001
- [14] Fabris L 2015 Gold-based SERS tags for biomedical imaging *J. Opt.* **17** 114002
- [15] Barchiesi D and Grosjes T 2015 Short note on the dipole approximation for electric field enhancement by small metallic nanoparticles. *J. Opt.* **17** 114003
- [16] Birke R and Lombardi J 2015 Simulation of SERS by a DFT study: a comparison of static and near-resonance Raman for 4-Mercaptopyridine on small Ag clusters *J. Opt.* **17** 114004
- [17] Muniz-Miranda M and Caporali S 2015 Surface-enhanced Raman scattering of ‘push–pull’ molecules: disperse orange 3 adsorbed on Au and Ag nanoparticles. *J. Opt.* **17** 114005
- [18] Bonhommeau S, Talaga D, Comesana-Hermo M, Ravaine S and Vallee R 2015 Colocalized dark-field scattering, atomic force and surface-enhanced Raman scattering microscopic imaging of single gold nanoparticles. *J. Opt.* **17** 114006
- [19] Farcau C, Vallee R, Boca S and Astilean S 2015 Polarized SERS on linear arrays of silver half-shells: sers re-radiation modulated by local density of optical states *J. Opt.* **17** 114007
- [20] Futamata M, Akai K and Lida C 2015 Gap mode Raman spectroscopy under attenuated total reflection geometry *J. Opt.* **17** 114008
- [21] Barchiesi D, Grosjes T, Colas F and Lamy de la Chapelle M 2015 Combined SPR and SERS: otto and kretschman configurations *J. Opt.* **17** 114009
- [22] Colas F, Barchiesi D, Kessentini S, Toury T and Lamy de la Chapelle M 2015 Comparison of adhesion layers of gold on silicate glasses for SERS detection. *J. Opt.* **17** 114010
- [23] Pavan Kumar G and Patra P V G A 2015 Geometry-dependent anti-stokes SERS radiation patterns from gold nanorod dimers *J. Opt.* **17** 114011
- [24] Guerrini L *et al* 2015 SERS efficiencies of micrometric polystyrene beads coated with gold and silver nanoparticles: the effect of nanoparticle size *J. Opt.* **17** 114012
- [25] Kah J, He S, Kang M, Khan F, Tan E and Reyes M A 2015 Optimizing gold nanostars as a colloid-based surface enhanced Raman scattering (SERS) substrate *J. Opt.* **17** 114013

- [26] Yao J *et al* 2015 Surface-enhanced Raman spectroscopy on single Fe₂O₃@Au spindle nanoparticle: polarization dependence and FDTD simulation *J. Opt.* **17** 114014
- [27] Chen H, Wen J, Zhang H, Zhang W and Chen J 2015 Stretchable plasmonic substrate with tunable resonances for surface-enhanced Raman spectroscopy *J. Opt.* **17** 114015
- [28] D'Andrea C *et al* 2015 Red shifted spectral dependence of the SERS enhancement in a random array of gold nanoparticles covered with a silica shell: extinction versus scattering *J. Opt.* **17** 114016
- [29] Haes A and Shrestha B 2015 Improving surface enhanced Raman signal reproducibility using gold-coated silver nanospheres encapsulated in silica membranes *J. Opt.* **17** 114017
- [30] Laurent G, Julien-Rabant C, Débarre A and Métivier R 2015 Single particle SERS signal on gold nanorods: comparative study of diarylethene photochromic isomers. *J. Opt.* **17** 114018
- [31] Cottat M *et al* 2015 Highly sensitive detection of paclitaxel by surface enhanced Raman scattering. *J. Opt.* **17** 114019
- [32] Xu S, Qi G, Jia Kq F C and Xu W 2015 A highly sensitive SERS sensor for quantitative analysis of glucose based on chemical etching of silver nanoparticles *J. Opt.* **17** 114020
- [33] Coluccio M L *et al* 2015 From nucleotides to DNA analysis by a SERS substrate of a self similar chain of silver nanospheres *J. Opt.* **17** 114021
- [34] Sim S J, Nguyen A and Lee J U 2015 Plasmonic coupling-dependent SERS of gold nanoparticles anchored on methylated DNA and detection of global DNA methylation in SERS-based platforms *J. Opt.* **17** 114022
- [35] Fujita K, Bando K, Smith N, Ando J and Kawata S 2015 Analysis of dynamic SERS spectra measured with a nanoparticle during intracellular transportation in 3D *J. Opt.* **17** 114023