

SURFACE-ENHANCED RAMAN SCATTERING FROM TRANSITION METALS AND BY ULTRA-VIOLET EXCITATION

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Abstract: This contribution reports some progresses on SERS from transition metal surfaces and in particular on the first ultraviolet SERS (UV-SERS) study. The enhancement in the UV region was calculated to be around two orders of magnitude for some transition metals.

Over the past three decades, surface-enhanced Raman spectroscopy (SERS) has gone through a tortuous pathway to develop into a powerful surface diagnostic technique. In 1974 Fleischmann, Hendra, and McQuillan performed the first measurement of a surface Raman spectrum from pyridine adsorbed on an electrochemically roughened silver electrode. After carefully making the calculation and experiment, Van Duyne and Jeanmaire claimed that the major contribution to the intense Raman signal is due to an enhancement of 10^5 - 10^6 times compared to the intensities predicted from the scattering cross section for the bulk pyridine. As a highly sensitive surface diagnostic technique, SERS had soon found its application in a wide variety of fields including electrochemistry, analytical chemistry, biology, catalysis, corrosion, environment protection etc. However, SERS had not developed as smoothly as many people had hoped to be a powerful and widely used technique. The biggest obstacle was that only three noble metals Au, Ag and Cu could provide large enhancement, which severely limited the widespread applications involving other metallic materials of both fundamental and practical importance. Many groups including ours have made great effort to search for new enhancing substrates. Since 1996, we have been developing several surface roughening procedures and optimizing the detection sensitivity of the confocal Raman microscope, then obtained good-quality SERS directly from net transition metals (e.g., Pt, Ru, Rh, Pd, Fe, Co and Ni and their alloys) [1,2]. The surface enhancement factor for transition metals was calculated, which ranged from one to four orders of magnitude [3]. Recently, based on this progress, we have successfully applied SERS in surface adsorption, electro-catalysis and corrosion of diverse transition metal-based substrates [4,5].

After extending the SERS study to many transition metals, we have been exploring the possibility of extending SERS to ultraviolet light excitation. Although about five thousand papers on SERS have been published, the excitation lines have only covered the visible spectrum up to the near-infrared region, from 450 to 1064 nm. Indeed, we have failed to obtain SERS from silver with ultra-violet excitation, in spite of the fact that silver is the best enhancers in the visible and near-infrared. Because the optical property of the transition metal is considerably different from that of silver and gold, it is worth it to test ultraviolet surface-enhanced Raman scattering (UV-SERS) of transition metals.

Very recently, we have obtained, for the first time, UV-SERS spectra from rough rhodium (Rh), cobalt (Co) and ruthenium (Ru) metal surfaces respectively. The experiments were carried out using a UV-vis R1000 Renishaw micro-Raman system equipped with a UV-enhanced CCD detector. The 325 nm laser line from the He-Cd laser was used for excitation. Pyridine, the most studied molecule in SERS was used to first test SERS on the roughened Rh electrode [6]. Then the UV-SER spectra of SCN^- and CO having small Raman cross sections were also obtained. The UV-SERS has also been observed from other transition metal electrodes such as Ru and Co. Although we were not able to obtain UV-SERS signal from the electrochemically roughened Pt electrode surface, however,

reasonably good UV-SERS signal from Pt nanoparticles has been obtained. It indicates that it is very important to prepare the substrates of a proper morphology and particle size in order to achieve good SERS activity also in the UV region.

The surface enhancement factor of the Rh electrode with the 325 nm excitation was calculated to be about two orders of magnitude using SCN⁻ as the probe ion. On the basis of the electromagnetic (EM) model, a simple calculation of the wavelength-dependent enhancement factor for Rh and Ag was carried out using the method described by Zeman and Schatz [7]. The enhanced field was calculated as a function of the particles size, aspect ratio and excitation wavelength. The result clearly revealed that the Rh spheroid nanoparticle has a much higher enhancement in the UV region compared with Ag, although the latter shows much higher enhancement in the visible region. This preliminary theoretical calculation is in agreement with the experimental data and provides a rationale to explain why some transition metals, instead of the typical SERS metals, may present observable SERS activity in the UV region.

It is worth of mentioning that because of surface selectivity, UV-SERS will have technique has more advantages in studying surface adsorption than other UV-Raman techniques, particularly in electrochemical systems. Furthermore, UV energies are close or to lie within the range of an electronic absorption of many macromolecules, more importantly, biomolecules, this will allow us to use UV-SERRS. Since the UV-Raman instrument is still at its infant stage, we still have a chance to improve the detection sensitivity. UV-SERS will be applied to a number of fields, including electrochemistry, biomedicines, catalysis, etc. Prospects and further developments in the SERS field will be discussed with emphasis on the emerging experimental methodology.

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