

RAMAN SPECTROSCOPY IN ELECTROCHEMISTRY

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Raman spectroscopy is a particularly useful technique for studying electrochemical surface reactions because it is a visible wavelength spectroscopy and permits in situ investigations. Most electrochemical systems can be studied by Surface Enhanced Raman Spectroscopy (SERS) which involves surface selection and preparation. The techniques involved in the preparation and observation of SERS signals have been highlighted in this review. Recent developments in the observation of SERS on non-SERS active substrates have also been reported. Studies on the various material - substrate systems have been listed. The application of SERS to various electrochemical systems is also reviewed.

Key words: Raman spectroscopy, surface enhancement, electrode surface roughening, In situ analytical technique

INTRODUCTION

Most electrochemical reactions take place at the electrode/electrolyte interface and hence these can be viewed as being essentially surface phenomena. Thus there is a need for techniques which can be used to study the surface chemical species and their interactions. It is with this purpose in mind that a vast array of surface sensitive spectroscopic techniques has been developed. Surface vibrational spectroscopies are particularly well suited to determine the chemical identity of adsorbed molecular species and to study their structure and orientation, the strength and nature of their bonds to the surface, the structure of surface active sites and the dynamics of surface chemical reactions in electrochemistry.

One of the inherent advantages of using vibrational spectroscopy to probe electrochemical interfaces is that the techniques permit in situ measurements and do not require special environments like vacuum or inert gas atmosphere for the sample. Raman spectroscopy is particularly useful because it is a visible wavelength spectroscopy, and aqueous medium which is a constituent of most electrochemical systems is transparent in this optical region. This is not true of other vibrational spectroscopies such as infrared spectroscopy (IRS) and this calls for special cell design.

In Raman spectroscopy, incident light is scattered by sample molecules and the change in frequency is measured. The difference in energy is either absorbed or given up by the molecular vibrations which are characteristic of the molecules. However the intensity of the signal is of the order of 10^{-7} of the incident beam and this requires particularly intense beams to be used as probe beams. The advent of lasers with highly intense monochromatic outputs gave a fillip to the application of this technique to electrochemical studies.

Signal enhancement

It is not easy to record Raman spectra from surfaces due to the small volume of the scatterers (10^{14} per cm^2). One of the methods used for overcoming the weak Raman signal from surfaces is the use of resonance conditions which give rise to Resonance Raman

Spectroscopy (RRS) [1,2]. This technique is limited to molecules which absorb strongly at the laser wavelength at which there is a resonance enhancement of the scattering cross-section leading to a strong output signal. The other technique is Surface Enhanced Raman Scattering (SERS) [3-5]. In this technique the cross-section for scattering is enhanced by several orders of magnitude for molecules adsorbed on pretreated surfaces. However, the use of these methods leads to difficulty in interpreting results because of normal mode and polarization selectivity in RRS, while there is incomplete understanding of SERS effects at present [6].

To detect unenhanced Raman spectra from surfaces, other approaches such as optical multichannel diode array (OMA) or the charge coupled device (CCD) camera can be used [6]. The OMA provides multiplex advantage and can detect signals of the order of 1 count/sec for monolayers on metal substrates [7,8]. The CCD camera has an order of magnitude quantum efficiency, can detect nearly every photon received because of very low dark currents and can work well in low background level environments and where time resolution is not needed [9]. The OMA allows one to record a substantial segment (ideally the entire spectrum) of the Raman spectrum simultaneously without wavelength scanning of the spectrometer which is useful when time resolution is needed [10]. Further by the use of suitable waveguide geometries such as asymmetric slab waveguide and integrated optical techniques [11] the signal can be enhanced.

Surface Enhanced Raman Scattering

The first study involving SERS [3] was carried out about a decade ago. The Raman spectrum of pyridine adsorbed on Ag electrode, which had been electrochemically roughened by current cycling in aqueous chloride solution was observed. Current cycling was effected to increase the surface area. Spectra of surprisingly good signal-to-noise ratios were obtained. A later experiment [12] revealed that optimization of surface treatment resulted in very large adsorbate intensities, much greater than could be accounted for by the increase in surface area. It was proposed that the phenomenon indicated an enhancement of the effective scattering cross section of

the adsorbate on the metal substrate.

It has been shown [13] that the SERS intensity depends on both macroscopic and atomic scale electrode surface roughness which in turn can be controlled by Oxidation-Reduction Cycles (ORC). It has also been observed that [12] SERS intensity depends critically on (i) electrode surface preparation, (ii) concentration of the sample in the bulk of the electrolyte, (iii) nature and concentration of the supporting electrolyte anion, and (iv) electrode potential. A later study [14] concluded that though all the above mentioned factors serve to enhance the SERS signal, they are not prerequisites for observing the signal.

SERS studies

SERS studies have been carried out on various substances adsorbed on a limited number of suitable metal substrates. The metal substrates which have been used are Ag, Au, Cu, Pt, Hg, Cd, Li, Ni and Pd. Studies on adsorption of benzene on TiO₂ [15] and some organic species on silver-coated teflon spheres [16] have been carried out, thus extending the range of substrates. Some of the organic species whose adsorption on various substrates have been investigated extensively are pyridine [3, 12, 13], cyanide [17-19], pythalocyanine [20-23], aniline [24-26], benzene [15, 27], piperidine [28], acetonitrile [29-30], phenanthroline [31], *p*-dimethylaminobenzonitrile [32], oxygen reduction catalysts such as Co-tetramethoxyphenylporphyrin [33] and cyclic amine complexes [34], polyaniline and polyaniline complexes [35], nucleic acid [36], and azide [37]. The adsorption of biologically important compounds [38] have also been studied and some of the compounds are proteins and porphyrins [39] and glucose oxidase [40].

The adsorption of inhibitors and the properties of coatings on metal surfaces have also been investigated by SERS. The adsorption of inhibitors on iron [41], on copper [42-44] and the physical properties of amine-modified polyoxyphenylene coatings electroformed on metal substrates [45] have been studied. In addition, the oxidation products on iron and iron-chromium alloys using Ag-overlayer [46] have also been studied by SERS. Anodic films formed on alloy of Ag and Cu [47] and on Ag and Cu [48, 49] in alkaline media and on HgTe [50] have been studied. One of the methods applied for extending the range of SERS active substrates on is by underpotential deposition [51-55]. SERS has been applied to high temperature/high pressure experimental systems with aqueous environments [56]. Electrochemical reaction mechanisms can also be elucidated by using this technique [57-60].

Surface preparation

Although a large number of SERS studies have been conducted, the mechanisms have not been uniquely identified. But there is general agreement that two major components are involved [53]: (i) enhancement of the electromagnetic field by the controlled roughening of the surfaces of metals that have appropriate dielectric properties (eg. Ag, Cu, Au); (ii) enhancement due to adatoms or clusters of atoms which may induce new electronic surface excitations or by resonance Raman scattering from adsorbates.

A pre-condition for observing SERS is the roughening of substrate by means of controlled oxidation-reduction cycle (ORC)

[61]. Such ORC procedures induce both macroscale (10-200nm) and atomic scale roughness. SERS active surfaces have also been produced by electroplating [62], evaporation [63], chemical reduction [64] and etching [65], although the signals are generally weaker than that obtained by ORC procedures. Very mild roughening of Ag surfaces which are chemically polished or controlled deposition of a few monolayers of Ag onto vitreous carbon or a semiconductor, all of which are restricted to a few monolayers, can induce SERS and it has been suggested that such treatment produces atomic scale roughness alone. These active sites are unstable and the SERS intensities decrease irreversibly, for example, by cathodic polarization at very negative potentials. Such intensity decreases have been attributed to migration of adatoms or groups of atoms to the edges of lattice planes.

Electrodes showing the effects of macroroughness only are produced by prolonged cathodic polarization at potentials below -1.6V or by repeated deposition and dissolution of underpotentially deposited (UPD) monolayers of metals such as Pb or Tl. These electrodes show diminished SERS (DSERS). The DSERS signals have a high stability, and enhanced Raman scattering can still be observed even on UPD and overpotential deposition (OPD) of foreign metals [52, 54]. Enhanced Raman signals cannot be detected on smooth silver surfaces, e.g. produced by polishing with alumina powder. Only Surface Unenhanced Raman Spectra (SUERS) can be detected using modulation together with signal averaging techniques from these surfaces.

Strongly enhanced signals can be detected from such polished surfaces by depositing small amounts of foreign metals like Ni, Co, Hg, Tl or Pb [51]. These metal adsorbates are deposited at underpotentials and are referred to as underpotential deposits (UPD). UPD technique can be utilised to deposit islands of a SERS active metal onto the surface of interest or thin metal layers of the sample material of interest on a suitable SERS active substrate. The objective in both cases is to engender SERS for adsorbates on the non-SERS material from the anticipated electromagnetic enhancement offered by nearby SERS-active moieties. The former approach has been attempted for Ag deposits on semiconductor surfaces, although it is not straight forward to identify the resulting SERS as arising from adsorbate on the semiconductor rather than on the deposited Ag itself. A useful variant of the latter approach involves the formation of UP deposited layers. Uniform deposits of up to a monolayer of a number of metals can readily be formed in this manner by using a suitable noble substrate. A virtue of this method of metal surface modification is the likelihood that the adsorptive properties will reflect chiefly those of the overlayer metal rather than the underlying substrate. Studies on the effect of UPD layers on the SERS active surface have shown that Raman signals are quenched in some cases even when the typical coverage is less than 10%.

Several investigations have shown that a large enhancement originates from the first adsorbed monolayer and subsequent monolayers provide a much smaller enhancement which may be ascribed to the electromagnetic mechanism; there exists also clear distinction in vibrational mode positions of the adsorbate for the first and subsequent monolayers. Among the substrates, the most

suitable one on which to produce UPD layers for SERS studies is gold. The extreme nobility of gold enables the formation of stable UPD layers even for metals having substantially positive UPD with respect to bulk deposition potential. Further the properties of the UPD layers on gold can be examined over a wide potential range including those potentials where there is a tendency for other anions or electron donor species to be adsorbed. Though the metals deposited by UPD are not themselves SERS active in the bulk state, yet intense SERS signals emanating with overlayers of UPD deposits, have been identified as arising from adsorbates bound to the overlayers rather than the underlying substrate. Thus UPD techniques provide a new approach for extending the applicability of SERS to other metal substrates that are not in themselves inherently SERS active.

The range of surfaces to which SERS can be applied has been extended to electrodeposited transition metal (Pt, Pd, and Rh) films on gold surfaces [55]. The adsorption and electrooxidation of CO on these surfaces has been investigated. These thin layers display characteristic electrochemical properties similar to the corresponding bulk metals.

APPLICATIONS

One of the important applications of SERS to electrochemical systems is the study of adsorption of inhibitors on metal surfaces. An investigation of adsorption of inhibitors on copper [42] showed that the undissociated inhibitors and their anions are adsorbed simultaneously with the surface concentration ratio depending on pH and electrode potential. SERS can also be used to study the nature of bonding of inhibitors to the metal surfaces. It has been shown that on iron [41], inhibitors form polymer-like films which are chemically bonded to the metal surface. Similarly the synergetic effects in the inhibition of copper corrosion with azole-type inhibitors has been studied using SERS [44]. SERS investigation of the amine-modified polyoxyphenylene coatings electroformed in situ on metal surfaces has shown that the properties of these coatings can be improved by the addition of surfactants which are dispersed throughout the coating and the substrate [45].

Raman spectroscopy has been used for identifying the various zinc species present in the zinc/bromide ion equilibrium complex in zinc-bromine model electrolytes for battery systems [57]. By using standard deconvolution/integration techniques along with published values, the amount of each zinc species could be quantitatively determined and the conductivity values explained.

The potential of SERS as an in situ molecular probe of interfacial redox processes arises from the ability to obtain vibrational spectra of interfacial species rapidly during an electrochemical reaction and to identify the intermediates by their characteristic interfacial vibration modes. Information on interfacial molecular transformations for multi-step reaction featuring adsorbed intermediates as well as on their structure and their orientation can also be obtained. The advantage of applying SERS to the study of interfacial processes is that the enhancement occurs in the interface itself, which discriminates strongly against influences from the more abundant ambient phase. The species electrogenerated during the

reduction of nitrobenzene at gold electrodes have been identified by the use of SERS [58].

One of the electrode reactions studied in detail is cyanide silver system. The reaction has been studied by simultaneous cyclic voltammetry and SERS measurements. The frequency of the C-N stretching vibration has been monitored while the potential was scanned from 0.5V to -1.0V. It has been shown from SERS spectra of cyanide adsorption in cyanide solution [19] that surface complex [66] of cyanide with electrode material (Ag) along with adsorbed water is formed. The complex is linear. Studies of cyanide adsorption in chloride solution suggests that cyanide interacts in end-bonded and side-bonded configurations [17]. Slow aggregation of the interfacial HCN occurs with passage of time [17].

Thus a majority of the results of these studies suggest that the SERS intensity-thin metal film coverage cannot be attributed to purely electromagnetic effects. The results obtained till now show that chemical effects such as adsorbate displacement and differences in the stabilization of SERS sites in the presence of different adsorbates have a role in determining the SERS intensity. An extensive list of atomic and molecular species that have been characterized by applying Raman spectroscopy electrochemical systems has been compiled recently [67]. Raman spectroscopy has proven to be a very powerful tool for obtaining information from adsorbates in electrochemical environments.

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