Surface enhanced Raman scattering from bare cobalt electrode surfaces

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Paper

Surface enhanced Raman spectra (SERS) of adsorbed species from a bare cobalt (Co) bulk electrode were observed for the first time with confocal Raman microscopy. A combined AFM, Raman and electrochemical study shows that a proper roughening procedure is vitally important for obtaining good-quality surface Raman spectra from the Co electrode. The surface enhancement factor ranges from 2 to 3 orders of magnitude, depending critically on the surface roughening procedure. The present study provides a bright prospect for the wide investigation of systems of practical application.

Introduction

Cobalt (Co) as a member of iron group metals is a very important transition metal.[1,2] This is not only due to its wide applications in electroplating and power sources and as a catalyst, but also due to its special magnetic properties, as used in data storage media.[3–6] In the past years, thousands of papers have been published each year related to this material indicating its great importance for research and everyday life.[2] As is well known, Co is a very active metal being very easily oxidized or corroded in air or electrolyte environments.[1,7,8] Therefore, it is essential to develop a thorough knowledge of the properties of the metal and related processes and mechanisms in various environments.

A wide variety of spectroscopic and conventional electrochemical techniques have been employed to study the processes on Co electrodes.[7–13] The former has some advantages over the latter in monitoring *in situ* the surface and interfacial processes at the molecular–atomic level. Although it is possible to investigate the surface oxide film of the Co in electrochemical environment by normal Raman spectroscopy,[14] the investigation of adsorbed molecule on the surface of monolayer amount is still a problem, especially without any enhancement. Surface-enhanced Raman scattering (SERS) has extremely high surface sensitivity for providing molecular level information in detail. Unfortunately, in the past two decades, this technique has been almost totally restricted to Ag, Au and Cu, which have the most pronounced SERS effect. In order to extend the surface Raman spectroscopic study to Co surface, two approaches have been made so far: (i) coating ultrathin Co film (several atomic monolayers) onto SERS active Ag electrodes.[15] SERS spectra of adsorbates (such as pyridine) on Co have been obtained with the aid of the long-range effect of the electromagnetic (EM) enhancement created by the SERS-active substrate underneath. However, in comparison with other transition metals, an ultrathin Co film with good uniformity on the rough surface is difficult to prepare and its stability and electrochemical reversibility over a wide potential range are quite poor. (ii) Depositing a rough and thick Co film with a few micrometers of thickness on a non-SERS active substrate such as glassy carbon, to make use of the SERS effect of the Co electrode itself.[16] However, the second approach has only recently worked successfully in our lab with the help of a confocal Raman microscope of very high detection sensitivity.

Surface Raman spectra of the adsorbed pyridine at the Co film electrodes have been obtained successfully.[16] However, the electrochemically deposited Co films may have some differences in the crystalline structure and other chemical and physical properties compared to the Co bulk phase formed by metallurgy. It would be of special interest if the surface Raman signals could be obtained directly from a bulk-phase Co electrode of widespread use. On the other hand, it is also important to ensure that the surface Raman spectroscopy can be extended to studies not only of pyridine as the SERS model molecule, but also of more general organic and inorganic molecules having a smaller Raman scattering cross-section. In this communication, we report a surface Raman spectroscopic study on adsorption at bare and bulk Co electrodes.

Experimental

Raman spectra were obtained using a confocal microprobe Raman system LabRam I. The 632.8 nm line from an internal He–Ne laser was used as the excitation line, the laser power on the electrode surface being about 12 mW. Prior to surface pretreatment, the Co electrode with diameter of about 2 mm was first mechanically polished with 0.3 and 0.05 μm alumina powder to a mirror finish followed by ultrasonic cleaning in Milli-Q water. The electrode was then subjected to a specific roughening treatment (which will be described in the following section) followed by thorough rinsing and transferring to the spectroelectrochemical cell for measurement. A large platinum ring served as the counter electrode. A detailed description of the spectroelectrochemical measurement has been given elsewhere.[17] AFM images of roughened Co surfaces were acquired on a NT-MDT SPM system solver (Russia). All the potentials were quoted *vs.* saturated calomel electrode SCE. All the chemicals used were analytical-reagent grade and the solutions were prepared using Milli-Q water.

Results and discussion

It has been found that the surface Raman signal from mechanically polished Co surface is extremely weak and is barely detectable even with a very long data acquisition time. It is therefore not feasible and of no practical significance to obtain surface Raman signal from this kind of surface. In view

of previous SERS studies on Au, Ag and Cu and the recent studies on Pt, Ni and Fe, a common strategy to increase the surface Raman signal from Co is to roughen the electrode to introduce a certain kind of surface roughness and hence to produce possible surface enhancement.[18] Thus, in order to obtain possible SERS from Co surfaces, we examined various surface-roughening procedures for Co electrodes to obtain surface spectra with better signal-to-noise ratio (S/N). Fig. 1 illustrates the impact of different surface-roughening procedure on the surface Raman intensity of pyridine adsorbed on Co electrode surfaces. After being well polished and cleaned with triply distilled water, the Co electrode was chemically etched in 1 M HNO$_3$ in the sonication bath for 10 min. As can be seen in Fig. 1a, the surface Raman signal is still quite weak, the signal for the stronger band (v_1, ring breathing mode) of pyridine is only about 15 counts per second (cps). In order to obtain stronger signals to make the SERS study of molecules of small Raman cross-section possible, the chemically etched Co electrode was subject to a further electrochemical post-treatment. By applying a double-step oxidation–reduction cycle (ORC) *ex situ* in 0.1 M KCl free of pyridine from −0.4 to +0.4 V for 3 s and then back to −0.4 V, a surface Raman signal as strong as 45 cps can be obtained. This is about 3 times stronger in intensity compared with that from the pure chemically etched Co surface. More surprisingly, if the Co electrode was further treated in 0.1 M KCl in the presence of 0.01 M pyridine in the spectroelectrochemical cell using the same roughening procedure (*in situ* ORC), a surface Raman signal of the adsorbed pyridine as strong as 250 cps can be obtained, see Fig. 1c. This illustrates that the proper surface-roughening procedure is necessary to obtain reasonably good Raman spectra for detailed investigations. However, the stability and reversibility of the *in situ* roughened Co electrode are still a problem to overcome.

Through further survey of the roughening methods, we found out that the Co electrode with reasonably high surface enhancement, good stability and uniformity can be obtained reproducibly by the combination of chemical etching (in 1 M HNO$_3$) and electrochemical roughening on the mechanically polished Co electrode (in 0.1 M NaClO$_4$ solution). The detailed roughening procedure is as follows: the mirror finish Co electrode was chemically etched for 20 s in a sonication bath followed by cathodic polarization at −1.4 V for hydrogen evolution to expel possible contaminations. Then the potential was increased to −1.2 V and kept for 20 s. After that, the potential was scanned to +1.0 V at a rate of 200 mV s^{-1} and returned to −1.25 V at a rate of 100 mV s^{-1}. The electrode was then kept under potential controlled at −1.25 V in the same solution until the Raman measurement.

In order to gain good understanding of the effect of various roughening pretreatments, the morphology of the chemically etched surface and the same surface after further electrochemical roughening has been characterized by AFM, as shown in Fig. 2.
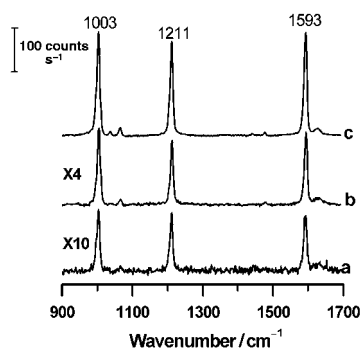
The AFM images show that the chemically etched surface (see Fig. 2a) is uneven, with some bumps of around 200 nm in diameter, while the surface roughened by electrochemical ORC (see Fig. 2b) is comparatively flat. However, the latter involves large bumps (about 2–5 μm on the entire surface), after zooming in the scanning range to each bumps, the AFM image can clearly identify the presence of bumps of around 100–300 nm. Although, except for the uniformity, significant difference can not be seen in the surface structure between the two electrodes, surface Raman signals do show big differences, indicating subtle differences in the surface microstructure obtained with various roughening methods. Using the unique method for calculating the surface-enhancement factor SEF based on the confocal Raman system,[19] we estimate that there are two to three orders of amplification for the Raman signal, depending on the surface-roughening procedure.

The good quality Raman signal thus obtained enables us to investigate the adsorption behavior of pyridine on the Co surface in detail. As can be seen in Fig. 3, the surface Raman signal increases as the potential moves negatively, and reaches its maximum at −1.2 V. At −1.3 V, the signal decreases, which may be due to the hydrogen evolution or the decomposition of the SERS active sites. The band at 241 cm^{-1} in the figure is from the Co–N vibration. This presents the unique advantage of Raman spectroscopy over infrared spectroscopy and the sum-frequency generation technique (SFG) in obtaining the substrate and adsorbate bonding information. The existence of the Co–N vibration in the whole potential range indicated that pyridine is adsorbed on the surface taking the end-on bonding configuration. However, the changes in the relative intensity of the 1006, 1213, and 1594 cm^{-1} bands imply a change in the surface structure or the enhancement mechanism. The relative intensity of the major bands is similar to that of Fe and Ni,
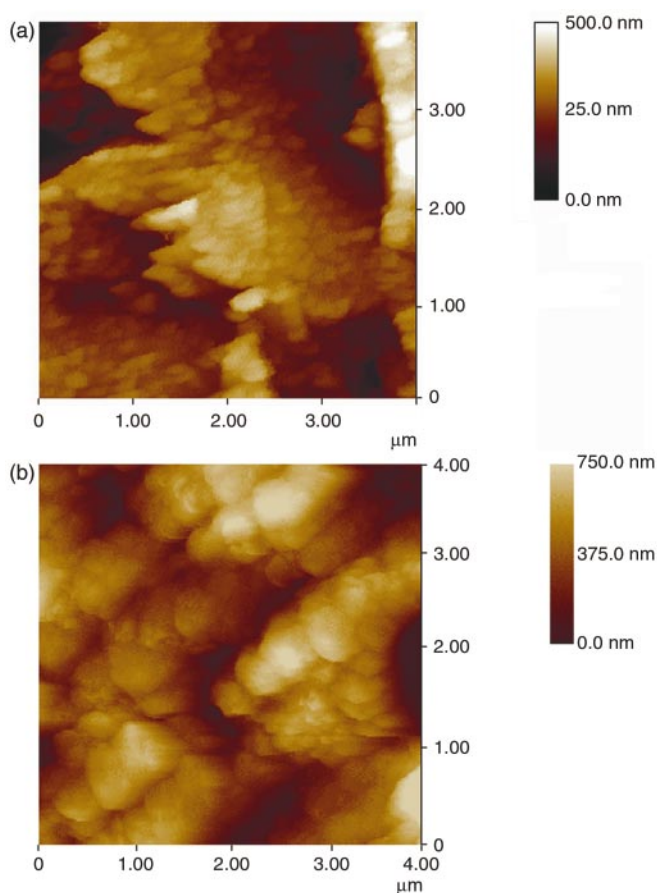

Fig. 2 The AFM images of Co surfaces roughened by (a) the chemical etching and (b) the chemical etching combined with electrochemical oxidation and reduction cycling (ORC).
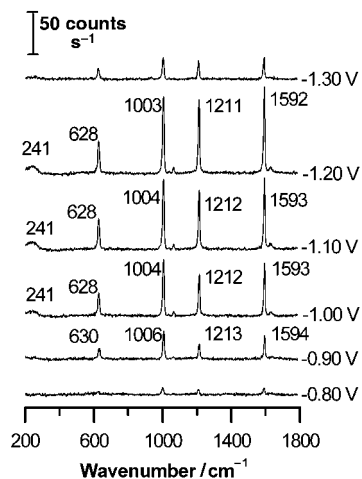

Fig. 1 The SERS spectra obtained at −1.2 V on cobalt electrodes after different pretreatments: (a) chemical etching; (b) *ex situ* ORC; (c) *in situ* ORC. The laser excitation line was 632.8 nm.

Fig. 3 The potential-dependent SERS spectra of the adsorbed pyridine from a cobalt electrode in 10^{-2} mol l^{-1} Py + 0.1 mol l^{-1} NaClO$_4$. The electrode was roughened by the electrochemical method. The laser excitation line was 632.8 nm.

however, distinctively different from that of the Pt and coinage metals.[20–23] A detailed discussion on this aspect will be given elsewhere.

To demonstrate the ability of surface Raman spectroscopy to study the adsorption at the molecular–atomic level *in situ*, benzonitrile (PhCN) was selected as sample molecule. PhCN, as a mono-substitute derivative of benzene, is a molecule of relatively high symmetry. Due to the special structure of the molecule, it can adsorb on the metal surface either through the benzene ring or the N end of the CN group, depending on the nature of the metal surface.[24–26] Fig. 4 presents the surface-enhanced Raman spectra of PhCN adsorbed on the roughened Co surface. The experiment was performed by moving the potential from the open-circuit potential (OCP, *ca.* −0.82 V) in a negative direction. At OCP, we can detect the bands at 1000, 1172, 1592, and 2210 cm^{-1}, corresponding to the ring breathing, the CH bending, ring stretching and the CN stretching vibrations, respectively. The very weak CN band and strong bands from the benzene ring indicate a parallel adsorption configuration. However, when the potential was moved to −1.00 V, the surface Raman signal was enhanced significantly. The most obvious change is the appearance of the band at 1640 cm^{-1}, the blue shift of the frequency of the 2210 cm^{-1} band to 2225 cm^{-1}. Although the CN band is quite strong, we could not detect the band of Co–N vibration, indicating that the sudden change of the Raman feature is not due to the change of the orientation from parallel to N-end adsorption. Furthermore, with the prolonged dwell-time, the Raman signal
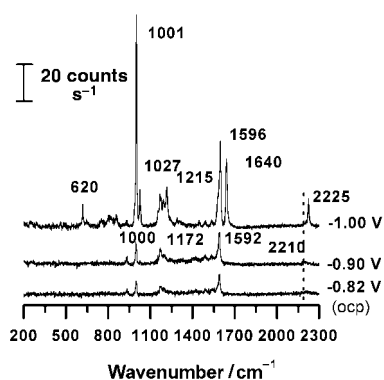
kept increasing in the following 10 min. It is very likely that the polymerization of PhCN occurred on the surface. It should be noted that the initial potential for the immersion of the Co electrode into the solution, and even the potential excursion direction, affect significantly the adsorption behavior of the PhCN on the surface. More detailed results and explanations will appear elsewhere. This study shows the possibility of using Raman spectroscopy for investigating the surface process on the Co surface.

In summary, using the appropriate surface-roughening procedures for Co electrodes together with the highly sensitive confocal microprobe Raman system we are able to obtain high-quality surface Raman spectra of pyridine and benzonitrile adsorbed at roughened Co electrodes over a wide potential range applied for the first time. Our preliminary results show that the confocal Raman microscopy will be a valuable tool for *in situ* investigation of the transition metal/liquid interfaces of practical importance, such as inhibition processes, mechanisms of corrosion and surface oxide film formation on Co surfaces.

Acknowledgements

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Fig. 4 The potential-dependent SERS spectra of benzonitrile on a rough cobalt surface in 0.02 mol l^{-1} benzonitrile + 0.1 mol l^{-1} NaClO$_4$. The experiment was done from the open circuit potential (OPC $\approx$ −0.82 V). The laser excitation line was 632.8 nm.