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Surface-Enhanced Raman Scattering (SERS) at Copper(I) Oxide

A. Kudelski,[1]* W. Grochala,[1] M. Janik-Czachor,[2] J. Bukowska,[1] A. Szummer[3] and M. Dolata[2]
[1] Department of Chemistry, University of Warsaw, Pasteur 1, 02-093 Warsaw, Poland.
[2] Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland
[3] Department of Materials Science, Technical University of Warsaw, Narbutta 85, 02-053 Warsaw, Poland

Surface-enhanced Raman scattering spectra of pyridine at a copper(I) oxide hydrosol and at Cu_2O-covered copper electrode produced by 'oscillating reaction roughening' are reported. It is shown that on such surfaces pyridine molecules adsorb as pyridinium cations. The 'oscillating reaction' pretreatment yields a passivated Cu surface which does not undergo any reduction during the cathodic scan, producing a SERS spectrum of pyridinium cations even after decreasing the electrode potential to strongly negative values. © 1998 John Wiley & Sons, Ltd.

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INTRODUCTION

Since it was discovered that Raman scattering from molecules adsorbed on certain surfaces is extremely enhanced, surface-enhanced Raman scattering (SERS) has become a well established technique for studying adsorbated molecule–substrate interactions. SERS signals have been observed from adsorbates on surfaces of metals such as Ag,[1,2] Au,[3] Cu,[4] Li,[5] Na,[6] K,[6] Rb,[6] Ti,[7], Co,[7] Ni,[8] Pd,[8] Pt,[9] Al,[10] Rh,[11] Cd,[12] Ga[13] and In[14]. In addition to these pure metals, SERS from molecules adsorbed on surfaces of oxides such as Ag_2O,[15] ZnO,[16] TiO_2,[16] α-Fe_2O_3,[17] Fe_3O_4,[18] NiO[19] and other compounds such as AgCl,[20] AgBr,[21] AgI,[22] GaP[23] and CdS[24] have been reported. The extension of SERS research to surfaces of other metals and compounds, particularly those which can be used in heterogeneous catalysis, will hopefully be pursued in the future.

In our previous work, we showed that SERS could be a useful method for studying the adsorption of molecules at catalysts containing copper microdomains.[25] X-ray microprobe analysis of a 40Cu–60Zr amorphous alloy after catalytic activation revealed the presence of oxygen at the surface.[25] Moreover, exposure of freshly cleaned copper to air produces a Cu_2O film[26] and EDS/X-ray microprobe analysis of a typical copper SERS-active substrate also showed that the copper surface is distinctly oxidized, oxygen being revealed mainly at the metallic 'particles' formed during SERS activation.[27] Therefore, in our recent development of SERS-active substrates, we have prepared Cu_2O hydrosol colloid.

This work is the first report on the SERS effect at a Cu_2O surface. A comparison between the SERS spectra of pyridine molecules adsorbed on a Cu_2O surface and on a copper SERS-active substrate was also made.

EXPERIMENTAL

The Raman spectra were recorded with a Cary 82 spectrometer equipped with a Lexel Model 98 krypton ion laser ($\lambda_{exc} = 647.1$ nm). The power at the sample was restricted to 40 mW. The spectral bandpass of the Raman spectrometer was 4 cm^{-1}. We use the 90° configuration, with an angle of incidence at the metal surface during SERS measurements of *ca.* 60°. The copper electrode was constructed from polycrystalline material (99.998% assay). A platinum sheet was used as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode; all potentials are reported *vs.* SCE.

The copper surfaces were characterized before the spectroelectrochemical measurements by optical microscopy, SEM (scanning electron microscopy) and X-ray electron microprobe analysis using a CAMECA instrument equipped with EDS (energy-dispersive spectrometric) and WDS (wavelength dispersive spectrometric) facilities.

H_2SO_4, NaOH, $CuSO_4$, $CuCl_2$, KCl, LiCl and glucose were all of analytical-reagent grade and were used as received. Pyridine (Ubichem, analytical-reagent grade) was distilled before measurements. Water was purified by triple distillation.

A Cu_2O suspension was prepared by mixing of 120 cm^3 of 0.6 M $CuSO_4$ solution and 8.7 cm^3 of 3 M glucose solution. The Cu_2O thus obtained was filtered, mixed at 35 °C with 60 g of 20% NaOH solution and after 1 h filtered and rinsed several times with triply distilled water. Cu_2O hydrosol containing pyridine was obtained from freshly prepared copper(I) oxide by heating with 0.05 M pyridine–0.1 M KCl solution until boiling, while

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* Correspondence to: A. Kudelski, Department of Chemistry, University of Warsaw, Pasteur 1, 02-093 Warsaw, Poland.
akudel@chem.uw.edu.pl

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stirring vigorously. Sedimentation of the oxide was prevented by the addition of starch.

Before spectroscopic measurements on polycrystalline copper surfaces, the following roughening pretreatments were applied: (i) 50 successive positive–negative scans at 20 mV s^{-1} in 0.2 M LiCl–0.01 M $CuCl_2$ solution from −0.55 to +0.05 V; and (ii) a new procedure (OR) based on an 'oscillating reaction roughening,' i.e. on pushing the system into an unstable state, where some anodic oscillations between the 'active' and the 'passive' states occur on a Cu electrode in 0.89 M H_2SO_4–0.89 M $CuSO_4$, at $E = E^0 + 0.4$ V (E^0 is the reversible potential of Cu in the above solution). This is a 'spontaneous' cycling of the system, alternative to procedure (i).

Details concerning the mechanism of the oscillating behaviour of the electrochemical systems[28] and in particular of those occurring in Cu/$CuSO_4$–H_2SO_4 are given elsewhere.[29–31]

From the technical viewpoint, the oscillating behaviour in our case was achieved as follows: an optional resistor *R* was introduced into the electrochemical circuit and was located in series with the working electrode. When the total resistivity of the electrolyte plus that of the optional resistor *R* had exceeded a threshold value, oscillations appeared.

RESULTS AND DISCUSSION

Figure 1 shows part of the Raman spectrum of pyridine adsorbed on a Cu_2O hydrosol surface from 0.05 M pyridine–0.1 M KCl solution [Fig. 1(a)] and the normal Raman spectrum of 0.05 M pyridine aqueous solution [Fig. 1(b)]. Comparison of these two spectra reveals that in Raman spectrum of pyridine adsorbed on Cu_2O two bands appear at 1005 and 1024 cm^{-1}, whereas in the normal Raman spectrum of pyridine solution there are two distinct bands at 1003 and 1035 cm^{-1}. Both the positions of the bands and the ratio of their intensities differ from those of pyridine in solution, indicating that we indeed are measuring the SERS spectrum of the Cu_2O surface. This spectrum is very weak, however indicating a relatively small enhancement factor as compared with the SERS spectrum recorded for pyridine adsorbed on the roughened Cu electrode surface [Fig. 1(c)]. Comparison between the band contours (a) and (b) in Fig. 1 indicates that bulk pyridine could contribute exclusively to the intensity of the 1005 cm^{-1} band in the SERS spectrum of pyridine adsorbed on Cu_2O sol. However, the band at 1024 cm^{-1}, which will be discussed further, is undoubtedly due to pyridine species adsorbed on Cu_2O particles.

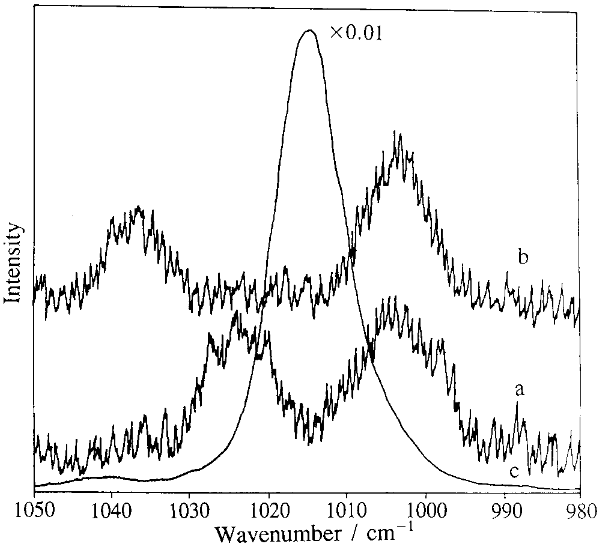

Figure 1. (a) SERS spectrum of pyridine adsorbed on Cu_2O hydrosol from 0.05 M pyridine–0.1 M KCl solution; (b) normal Raman spectrum of 0.05 M pyridine aqueous solution; (c) SERS spectrum of pyridine adsorbed on a Cu electrode from 0.05 M pyridine–0.1 M KCl solution ($E = -1.0$ V). Cu roughened with the standard procedure (i).

The SERS spectrum of pyridine adsorbed on the typical SERS-active copper substrate is shown in Fig. 1(c). As follows from a comparison of Fig. 1(a) and (c), these SERS spectra differ distinctly from one another. This implies that, at least in one case, there is a strong specific (chemical) adsorption and/or protonation of the adsorbed pyridine molecules (chemical modification) and/or the orientation of the adsorbed pyridine molecules is different in both cases.

To ascribe the SERS spectrum of pyridine on Cu_2O to an appropriate form of adsorbed pyridine we compared our SERS spectrum [Fig. 1(a)] with the spectra of pyridine on various substrates reported in the literature. We found that our SERS spectrum resembles either that of pyridine on a silver electrode in contact with acidic solution or the SERS spectrum observed at the silver electrode roughened electrochemically in the presence of pyridine (e.g. see Fig. 1 in Ref. 32).

The origin of these bands (especially that at 1024 cm^{-1}) is still uncertain. Howard *et al.*[33] attributed the 1025 cm^{-1} band to an insoluble pyridine complex of silver(I) chloride. Fleischmann and Hill[34] assigned it to strongly chemisorbed pyridine. Many investigations were performed in acidic solutions and it has been proposed that the 1025 cm^{-1} band is due to the pyridinium ion or pyridinium chloride adsorbed on the silver electrode.[35–38] Saito[32] suggested that the 1025 cm^{-1} band appearing on dilution in neutral solution has the same origin as the 1025 cm^{-1} band which appeared on acidification and attributed the origin of this band to a silver–pyridine–halide complex.

Certainly we could not exclude the formation of a copper(I)–pyridine complex. However, as follows from the literature data, various molecules do adsorb on metal oxides in protonated forms.[16,18] For example, Mou *et al.*[18] found that SERS spectra of tetraphenylporphyrin (H_2TSPP) on Fe_2O_4 infer its diacid form (H_4^{2+}TSPP) at the surface. Moreover, Yamada and Yamamoto[16] suggested that pyridine adsorbs on ZnO and TiO_2 surfaces in a protonated form. Therefore, we ascribe the observed SERS spectrum [Fig. 1(a)] to the pyridinium cation.

The affinity level of pyridinium cation adsorbed on Ag is lowered appreciably (0.8 eV) compared with that of adsorbed pyridine.[39] Therefore, an important difference between the SERS spectrum of pyridinium cation and that of the neutral pyridine molecule, which would confirm that the 1024 cm^{-1} band originates from the adsorbed pyridinium cation rather than from strongly chemically adsorbed pyridine, is that the maximum of the charge-transfer (CT) effect for the cation is expected to appear at an electrode potential more positive than that for neutral pyridine. The slope of a plot of excitation energy *vs.* potential, for which the maximum SERS intensity is observed, for pyridine adsorbed on Cu from 0.05 M pyridine–0.1 M KCl solution was determined as 1.85 eV V^{-1}.[40] Using this value we could roughly estimate that the position of the CT effect for the pyridine cation should be shifted by about 0.45 V towards more positive potentials. Since for pyridine adsorbed on Cu a maximum of the CT effect is observed near -1.0 V (Fig. 2), we would expect the corresponding maximum for the pyridinium cation to appear near -0.55 V.

The potential at which the CT enhancement reaches its maximum can be determined from the dependence of the SERS intensity on electrode potential under the assumption that changes in the surface coverage and in the orientation of the molecules do not produce any new maxima.

To measure the dependence of the SERS spectra on a Cu_2O surface on the electrode potential, we produced a Cu surface covered with a Cu_2O layer.

Figure 3 shows the surface morphology of Cu roughened with the new procedure based on the 'oscillating reaction (OR) roughening' [procedure (ii)]. One can see that the surface is etched, showing 'strips' between the distinctly etched grain boundaries. Some small, roundish particles are visible. The surface looks very different from the common 'bumpy,' SERS-active metal surface.[41] It is, however, similar to that obtained by rapid anodic etching of Cu.[27] Figure 4 shows a typical WDS spectrum taken from the surface presented in Fig. 3. A distinct signal of O suggests that the OR pretreatment (and the subsequent air exposure) provides an oxidized/passivated Cu surface, as required.

Figure 5 shows part of the SERS spectrum of pyridine on such a surface obtained by OR roughening. The SERS spectrum shown in Fig. 5 resembles that of pyridine adsorbed on Cu_2O [Fig. 1(a)] but is significantly different from that of 0.05 M pyridine solution [Fig. 1(b)]. A comparison of the SERS spectra in Figs 1(c) and 5 indicates that the contribution from the surface plasmon enhancement is considerably smaller for the OR (ii) oxidized Cu surface than for Cu surface roughened according to the commonly used pretreatment (i).

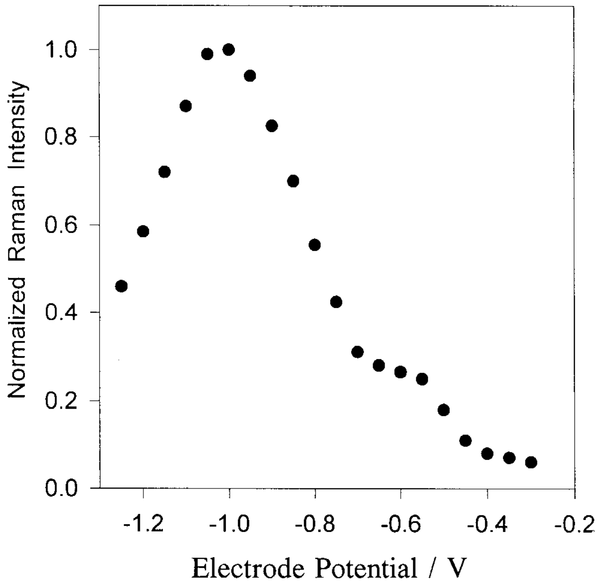

Figure 2. Potential dependence of the Raman intensity of the 1015 cm^{-1} band of pyridine adsorbed on a Cu electrode from 0.05 M pyridine–0.1 M KCl solution.

Figure 3. Typical morphology of Cu surface after the roughening according to the new OR procedure (ii), when the electrode is oscillating between both the active and the passive state. Magnification 1000 ×.

The potential dependence of the SERS spectrum for the surface roughened by the OR procedure exhibits a maximum at *ca.* $E = -0.5$ V, corresponding to the maximum of CT enhancement for this system, as discussed above (see Fig. 6). This maximum cannot be ascribed to the reduction of copper oxides because in such a case copper clusters would be produced and the SERS spectrum exhibiting a single band at 1015 cm^{-1}

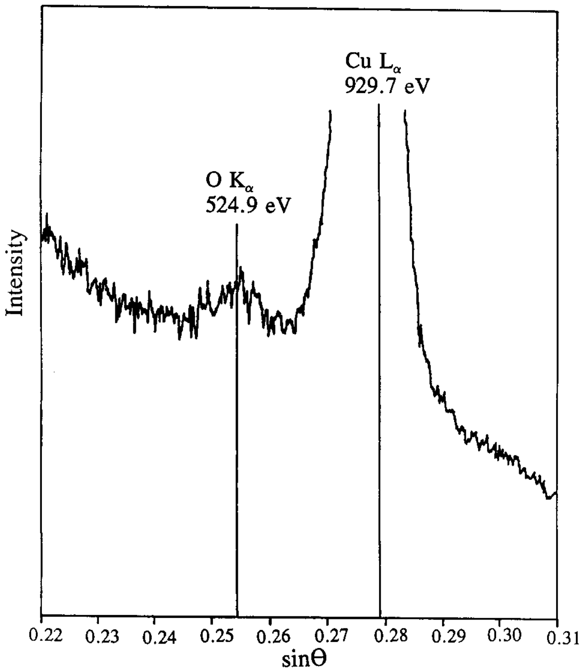

Figure 4. WDS/X-ray microprobe analysis showing presence of O and Cu at the surface after pretreatment (ii). Apparently the Cu surface is passivated as the weak O signal suggests.

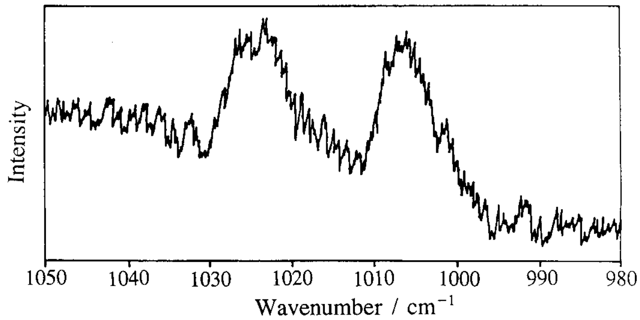

Figure 5. SERS spectrum of pyridine adsorbed from 0.05 M pyridine–0.1 M KCl solution on the Cu surface after the new OR procedure $E = -0.55$ V.

of high intensity would appear. No such situation was observed; the SERS spectrum consists of two bands in the whole electrode potential range examined (down to -1.0 V). Hence the observed difference (0.5 V) between the electrode potentials of the CT maximum for pyridine adsorbed on Cu and on Cu_2O supports our suggestion that the pyridinium cation rather than a neutral pyridine molecule adsorbs on the Cu_2O surface.

The question arises of why we do not see a band at *ca.* 1015 cm^{-1} indicative of adsorption of pyridine on metallic Cu [Fig. 1(c)], when measuring the SERS spectra on Cu roughened with the OR (ii) pretreatment, even after decreasing the electrode potential to -1.0 V. In order to answer this question, one has to take into account that we complete our OR pretreatment (ii) while the surface is still oxidized/passivated, in the passive state, at the lowest current density occurring during the oscillations. Our Cu surface, after the OR pretreatment, carries an oxide film. Apparently this film does not have a tendency to undergo any reduction during a cathodic scan; we do not see any cathodic reduction current in the cyclic voltammogram.

It is worth mentioning that Raman bands characteristic of pyridine adsorbed on Cu_2O can also be recorded on a Cu surface roughened by a standard procedure in LiCl–$CuCl_2$ solution.[27] Figure 7 shows the evolution of the SERS spectra of pyridine on a typically roughened Cu surface at electrode potentials $E = -0.25$, -0.35 and -0.45 V (the open-circuit potential was $E_{stat} = -0.23$ V). The SERS spectrum at $E = -0.25$ V consists of two bands at 1005 and 1021 cm^{-1}, whereas at $E = -0.45$ V only one broad and strong band at 1015 cm^{-1} is visible. This band is characteristic of pyridine on a Cu surface. We presume that the observed evolution of the SERS spectra is due to the reduction of copper(I) oxide to copper(0) and the subsequent creation of some 'active sites,' resulting in a simultaneous change of the species adsorbed from pyridinium cation to pyridine molecule.

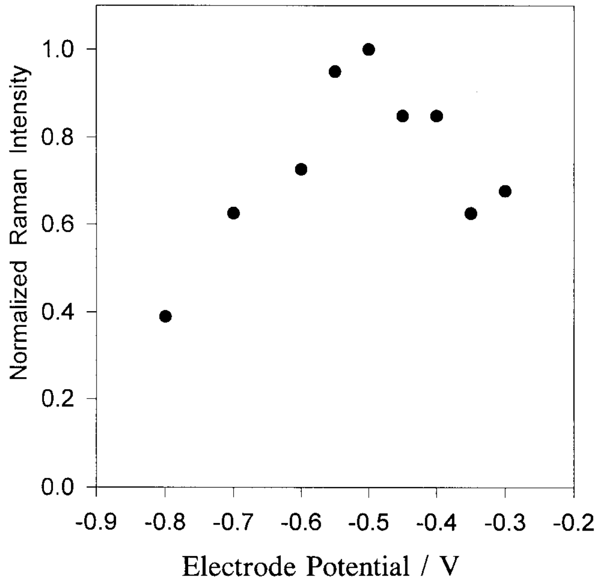

Figure 6. Potential dependence of the Raman intensity of the 1024 cm^{-1} band of pyridine adsorbed from 0.05 M pyridine–0.1 M KCl solution on the Cu surface roughened with the new OR pretreatment.

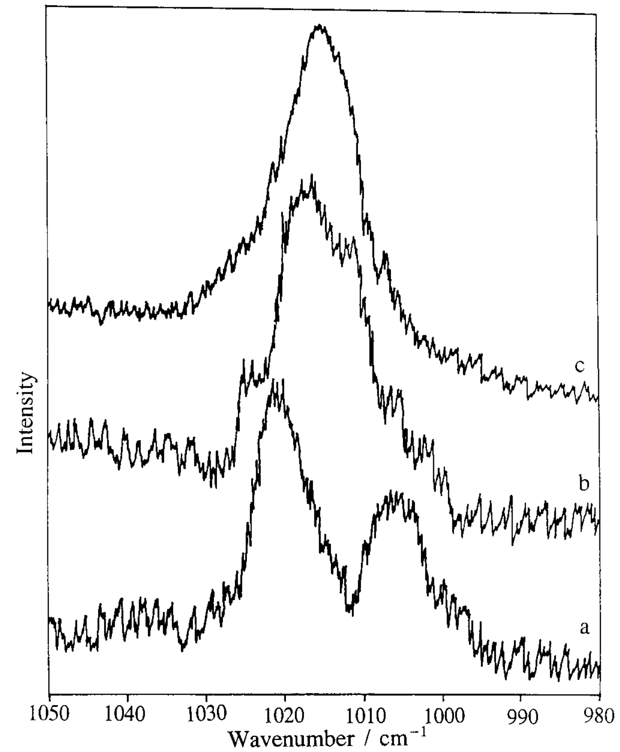

Figure 7. Evolution of the SERS spectra of pyridine adsorbed from 0.05 M pyridine–0.1 M KCl solution on the Cu surface roughened by standard procedure in LiCl–$CuCl_2$ solution. (a) $E = -0.25$ V; (b) $E = -0.35$ V; (c) $E = -0.45$ V.

CONCLUSION

This is the first study in which SERS of pyridine on Cu_2O has been observed both on hydrosol particles and on a copper(I) oxide-covered Cu electrode. Our results suggest that pyridine molecules are exclusively adsorbed on such surfaces as pyridinium cations. Since copper SERS-active electrodes are usually distinctly oxidized, the pyridinium cation spectrum may disturb both the SERS spectrum of pyridine (especially at less negative potentials, see Fig. 7) and the shape of the Raman intensity *vs.* electrode potential plots, by introducing an additional CT maximum near -0.5 V *vs.* SCE (see Fig. 2).

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REFERENCES

1. M. Fleishchmann, P. J. Hendra and A. J. McQuillan, *Chem. Phys. Lett.* **26**, 163 (1974).
2. D. L. Jeanmaire and R. P. Van Duyne, *J. Electroanal. Chem.* **84**, 1 (1997).
3. U. Wenning, B. Pettinger and H. Wetzel, *Chem. Phys. Lett.* **70**, 49 (1980).
4. B. Pettinger and H. Wetzel, *Ber. Bunsenges. Phys. Chem.* **85**, 473 (1981).
5. M. Moskovits and D. P. DiLella, in *Surface Enhanced Raman Scattering*, edited by R. K. Chang and T. E. Furtak, p. 243. Plenum Press, New York (1982).
6. B. Bozlee, B. Lian, J. Kahn, R. L. Garrell, T. Herne, A. Leiden, P. Palko, N. Hess and G. Exarhos, *Chem. Phys. Lett.* **196**, 437 (1992).
7. H. Seki, *J. Electron Spectrosc.* **39**, 289 (1986).
8. H. Yamada, Y. Yamamoto and N. Tani, *Chem. Phys. Lett.* **86**, 397 (1982).
9. W. Krasser and A. J. Renouprez, *Solid State Commun.* **41**, 231 (1982).
10. P. F. Liao and M. B. Stern, *Opt. Lett.* **7**, 483 (1982).
11. W. L. Parker, R. M. Hexter and A. R. Siedle, *Chem. Phys. Lett.* **107**, 96 (1984).
12. B. H. Loo, *J. Chem. Phys.* **75**, 5955 (1981).
13. D. P. Dilella and P. Zhou, *Chem. Phys. Lett.* **166**, 240 (1990).
14. C. Jennings, R. Aroca, A.-M. Hor and R. O. Loutfy, *Anal. Chem.* **56**, 2033 (1984).
15. Y.-S. Li, *J. Raman Spectrosc.* **25**, 795 (1994).
16. H. Yamada and Y. Yamamoto, *Surf. Sci.* **134**, 71 (1983).
17. P. Zhang, Y. Wang, T. He, B. Zhang, X. Wang, H. Xin and F. Liu, *Chem. Phys. Lett.* **153**, 215 (1988).
18. C. Mou, T. He, X. Wang, F. Liu, J. Jiang and L. Chen, *Wuli Huaxue Xuebao*, **12**, 841 (1996).
19. B. H. Loo, *J. Electroanal. Chem.* **136**, 209 (1982).
20. X. Gao, C. Wan, T. He, J. Li, H. Xin and F.-C. Liu, *Chem. Phys. Lett.* **112**, 465 (1984).
21. J. Wang, D. Li, H. Xin, S. Xu and F.-C. Liu, *Spectrochim. Acta, Part A* **43**, 375 (1987).
22. C. Mou, D. Chen, X. Wang, B. Zhang, T. He, H. Xin and F.-C. Liu, *Spectrochim. Acta, Part A* **47**, 1575 (1991).
23. S. Hayashi, R. Koh, Y. Ichiyama and K. Yamamoto, *Phys. Rev. Lett.* **60**, 1085 (1988).
24. T. Li and J. Chen, *Ganguang Kexue Yu Kuang Huaxue* **4**, 30 (1988).
25. J. Bukowska, A. Kudelski and M. Janik-Czachor, *Chem. Phys. Lett.* **268**, 481 (1997).
26. T. Hashemi and C. A. Hogarth, *Electrochim. Acta* **33**, 1123 (1988).
27. A. Kudelski, J. Bukowska, M. Janik-Czachor, W. Grochala, A. Szummer and M. Dolata, *Vib. Spectrosc.* in press.
28. J. L. Hudson and T. T. Tsotsis, *Chem. Eng. Sci.* **49**, 1493 (1994).
29. A. L. Kawczyński, M. Przasnyski and B. Baranowski, *J. Electroanal. Chem.* **179**, 285 (1984).
30. A. L. Kawczyński, W. Raczyński and B. Baranowski, *Z. Phys. Chem.* **269**, 596 (1988).
31. M. Dolata and A. L. Kawczyński, *Pol. J. Chem.* **71**, 1699 (1997).
32. H. Saito, *J. Raman Spectrosc.* **24**, 191 (1993).
33. M. W. Howard, R. P. Coony and A. J. McQuillan, *J. Raman Spectrosc.* **9**, 273 (1980).
34. M. Fleischmann and I. R. Hill, *J. Electroanal. Chem.* **146**, 353 (1983).
35. R. L. Birke, I. Bernard, L. A. Sanchez and J. R. Lombardi, *J. Electroanal. Chem.* **150**, 447 (1983).
36. D. J. Rogers, S. D. Luck, D. E. Irish, D. A. Guzonas and G. F. Atkinson, *J. Electroanal. Chem.* **167**, 237 (1984).
37. H. Chang and K. C. Hwang, *J. Am. Chem. Soc.* **106**, 6586 (1984).
38. S. C. Sun, I. Bernard, R. L. Birke and J. R. Lombardi, *J. Electroanal. Chem.* **196**, 359 (1985).
39. M. Kobayashi and M. Imai, *Surf. Sci.* **158**, 275 (1985).
40. J. C. Ingram and J. E. Pemberton, *Langmuir* **8**, 2034 (1992).
41. S. Schultz, M. Janik-Czachor and R. P. Van Duyne, *Surf. Sci.* **104**, 419 (1981).