

Surface-Enhanced Raman Scattering from Bare Zn Electrode

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Using confocal Raman microscopy, potential dependent surface-enhanced Raman spectra (SERS) of pyridine adsorbed on a bare zinc (Zn) bulk electrode were observed for the first time, and the adsorption behavior of pyridine on zinc was discussed. An electrochemical oxidation–reduction method was employed to roughen Zn electrodes for creating SERS. Related SEM measurement was performed to obtain the morphological information of the roughened electrode for understanding the SERS mechanism on it. An enhancement factor of around two orders of magnitude for pyridine adsorbed on a roughened Zn electrode was estimated.

1. Introduction

Due to its high specific energy density, high hydrogen overpotential, low cost, and ease of handling, zinc has been used extensively as an electrode for primary and secondary batteries (Zn–Ni, Zn–air, Zn–Ag, and Zn–MnO₂ batteries, etc.).^{1–4} Zinc is more active than iron, and it can be easily oxidized in the air or some corrosive environment, so it is often used as a sacrificial protective coating to prevent corrosion of steel (galvanized steel) exposed to water. A large number of conventional electrochemical and spectroscopic techniques have been employed to study the corrosion behavior of zinc in neutral solutions or a humid atmosphere and its passivation in alkaline electrolytes.^{5–9}

However, conventional electrochemical techniques can only tell the overall information about the reactions on electrodes. Spectroscopic techniques, especially the in situ ones, are outstanding for studying metal/solution interfaces at the molecular/atomic level, which is more advantageous in understanding the essence of the process related to the metal. Surface-enhanced Raman spectroscopy (SERS) has been developed as a useful in situ tool for providing bonding information between adsorbates and substrates since it was originally found in 1970s. During last 30 years, numerous researchers in this field have been making efforts to extend its application due to its high sensitivity and selectivity.^{10–13} Tian's group¹⁴ has successfully extended SERS to various transition metals such as Pt, Fe, Co, Ni, Rh, Ru, and Pd, etc. during the past decade.

For zinc, research, in about the 1980s, concerning SERS on Cd and Hg^{15,16} led people to assume that zinc metal is likely to have a SERS effect, but until now there have been no reports on SERS studies from a bare Zn electrode. Raman spectra of CN[–] adsorbed on thin Zn layers deposited from cyanide plating baths onto a silver substrate had been obtained by Fleischmann et al.¹⁷ Recently, Cai et al.¹⁸ electrodeposited silver on Zn electrodes to enhance the rather weak Raman signal of a passive film for studying the behavior of zinc electrodes in alkaline solutions. It was found that this procedure was effective for

experiments performed in the more dilute KOH solutions, that is, 0.1 mol/L, but the attempts to use it for more concentrated KOH solutions were not very successful because of the lack of adherence of the Ag particles to the substrate. This is not appropriate for studying surface adsorption because one cannot ensure that adsorbate was only adsorbed at the zinc surface and excluded the great enhancement of Ag. It is apparent that the most convincing and challenging method is to obtain SERS from the bare metal surface directly. Here, we present a study of surface Raman spectroscopy from bare Zn electrode using a proper roughening process.

2. Experimental Section

The spectroelectrochemical cell used has been described elsewhere.¹⁹ A polycrystalline Zn (99.99%, ca. 2 mm diameter) rod embedded in a Teflon sheath was used as the working electrode, a large platinum ring served as the counter electrode, and a saturated calomel electrode (SCE) served as the reference electrode. All the potentials were versus SCE. The Zn electrode was polished with 3 μ m, 0.3 μ m, and 0.05 μ m alumina powder successively, followed by ultrasonic cleaning to a mirror finish. Then, the electrode was roughened in an electrochemical cell, rinsed thoroughly with Milli-Q water, and finally transferred to the spectroelectrochemical cell for Raman experiments.

Raman spectra were obtained using a confocal microprobe Raman system (LabRam I, Dilor) that has been described in detail elsewhere.²⁰ A long working distance 50 \times objective was used to collect the Raman scattering signal. The excitation wavelength was 632.8 nm from a He–Ne laser with a laser power of about 8 mW at the sample surface. The slit and hole sizes were 200 and 800 nm, respectively. SEM images of roughened Zn electrodes were taken with a field-emission microscope (Leo, 1530) operated at an accelerating voltage of 20 kV.

All the chemicals used were analytical reagents and the solutions were prepared with Milli-Q water.

3. Results and Discussion

In our previous study, we have found that different surface pretreatment of the metal surface greatly influences the surface enhancement effect of the metal substrates. Therefore, we first examine the influence of different surface pretreatments of the

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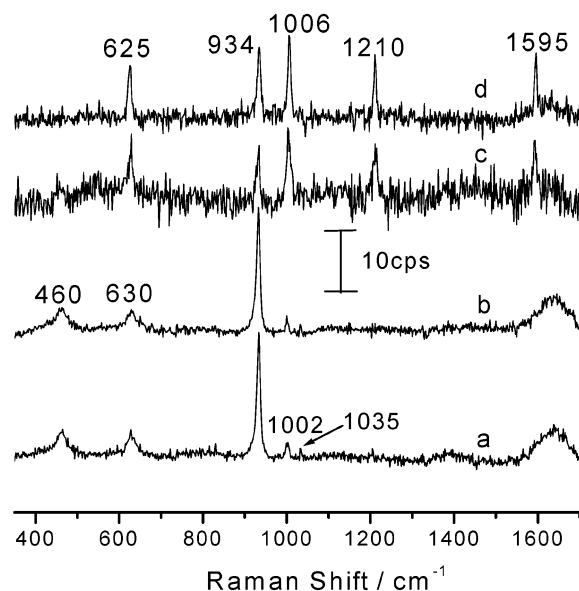


Figure 1. Raman spectra of pyridine (a) in the bulk solution and adsorbed on Zn surfaces at -1.4 V with different treatments: (b) mechanical polishing, (c) ex situ ORC by a double step method, (d) ex situ ORC by a linear sweep ORC method. Acquisition time: 20 s (c,d); 200 s (a,b).

surface Raman spectra of adsorbed species on the surfaces, the Raman spectra were shown in Figure 1.

The Raman spectrum obtained from a mechanically polished Zn electrode shows essentially the same Raman feature as the solution species in Figure 1a. The peaks at 460, 630, and 934 cm^{-1} come from ClO_4^- , and the relatively weak peaks at 1002 and 1035 cm^{-1} are signals of pyridine in solution. There is no observable signal from the surface species. Therefore, to obtain the surface Raman signal from Zn electrodes, one has to roughen the surface.

It has been reported that chemical etching, the electrochemical oxidation–reduction cycle (ORC), or the combination of them can be used effectively for the roughening of transition metals such as Fe,²¹ Co,²² Ni,²³ etc. Chemical etching has been considered as the simplest method for creating a SERS-active substrate; therefore, as the first try, we used H_2SO_4 solution to roughen Zn electrodes. Unfortunately, no discernible surface Raman signal of pyridine can be observed. As an alternative way to roughen the metal surface, one can use the electrochemical ORC method. During the electrochemical roughening processes, the potential function applied to the electrode will greatly influence the resulting structure of the electrode surface. Two methods, the linear sweep method and the double step method, have been found that can roughen effectively the Zn electrode while presenting reasonable SERS activity. In both methods, a NaClO_4 neutral solution was used as the electrolyte. The linear sweep is to sweep the potential of the Zn electrode between -1.6 and -0.7 V at a rate of $50 \text{ mV}\cdot\text{s}^{-1}$ for several cycles to allow the oxidation and reduction of the electrode surface. Finally, the electrode was held at -1.6 V for several minutes to reduce the zinc oxide on the surface completely (Figure 2a). A detailed analysis of the cyclic voltammetric behavior of zinc in this solution has been reported by Hassan.²⁴ Raman spectrum d in Figure 1 is obtained from this surface at the potential of -1.35 V on Zn electrode. The four peaks located at ca. 625, 1006, 1210, and 1595 cm^{-1} are attributed to the vibrations of the ring in-plane deforming (ν_{6a}), totally symmetric ring breathing (ν_1), C–H in-plane deforming (ν_{9a}), and ring stretching (ν_{8a}), respectively. In the second method, the electrode

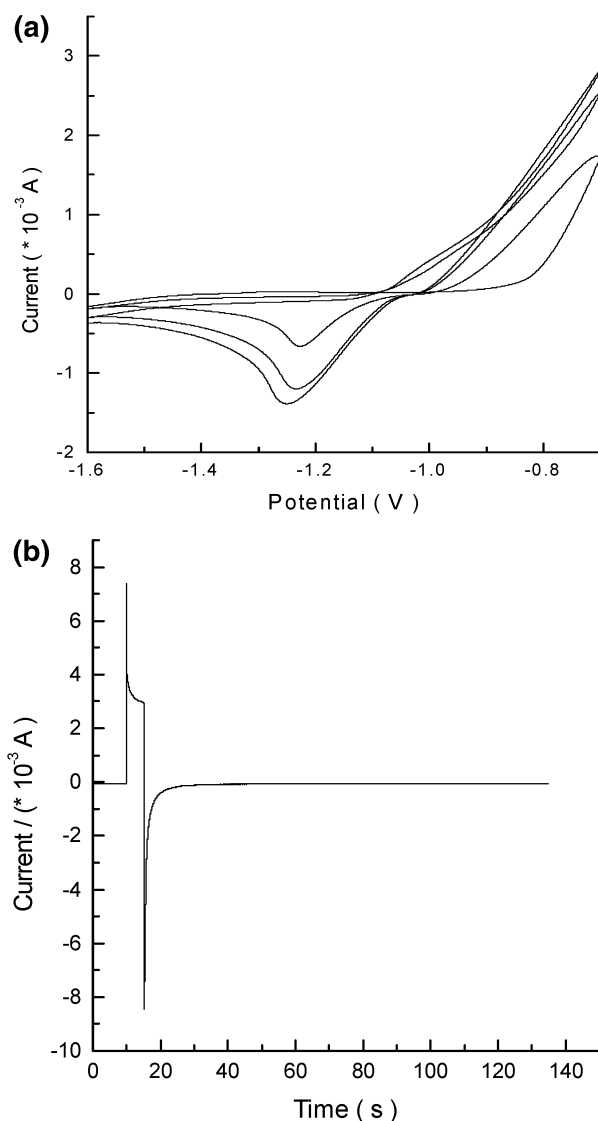


Figure 2. Two electrochemical roughening procedures for Zn electrodes in 0.5 M NaClO_4 solution: (a) a linear sweep ORC with a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$. (b) a double step ORC.

potential was stepped from a initial potential of -1.6 to -0.7 V and kept for 5 s and then stepped back -1.6 V for the thorough reduction of the surface oxide (Figure 2b). We also get an enhanced Raman signal of pyridine on this surface as shown in Figure 1c, but it is visibly not so good in intensity and quality in comparison with Figure 1d. These two different roughened Zn surfaces have similar bluish black appearances, and Figure 3 gives the SEM images of them. Inspection of the SEM images demonstrates that the size of particles for both the electrodes is, on average, 100–200 nm in diameter with some additional larger bumps that may be due to the aggregation of several smaller ones. This size distribution is very similar with other roughened transition metal electrodes with high SERS activity.¹⁴ Figure 2b shows that the anodic change is not recovered in the cathodic process. This may be the reason that the potential step ORC is not as good as the potential sweep ORC method. Thus, in the following experiments, linear sweep ORC was chosen to roughen Zn electrode.

Figure 4 shows a set of potential dependent Raman spectra of pyridine adsorbed on a roughened Zn electrode in 0.01 M pyridine + 0.1 M NaClO_4 solution. The experiment was done stepwise from negative to positive potentials. No observable Raman signal can be observed at -1.6 V, and a very weak

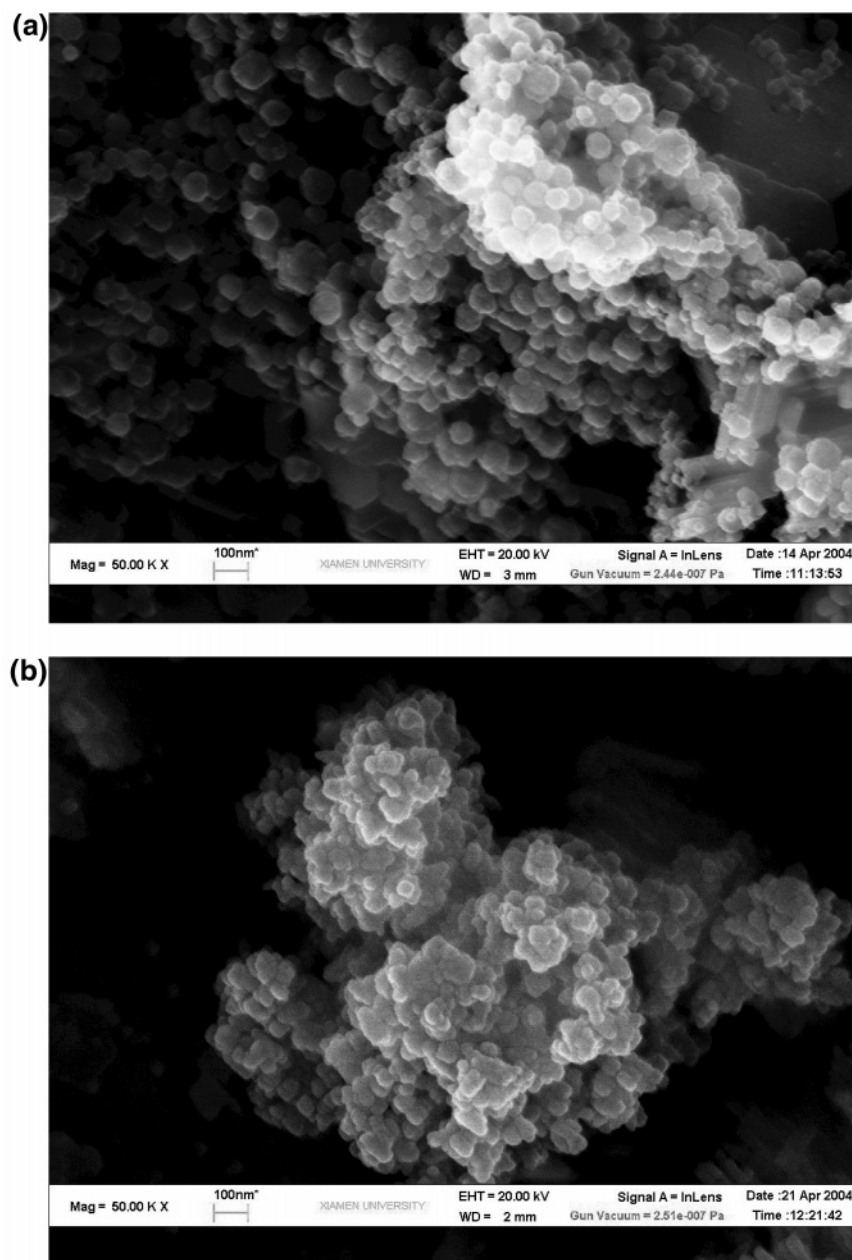


Figure 3. SEM images of Zn electrode surfaces roughened by (a) linear sweep ORC and (b) a double step ORC.

surface signal can be observed from the solution background. The surface signal reaches its maximum at -1.35 V with an intensity of the ν_1 mode at about 10 cps. As the potential shifts positively to -1.3 V, a new broad band at ca. 546 cm^{-1} appears accompanied by a decrease of intensity of adsorbed pyridine. This band can be assigned to the zinc oxides on the Zn surface according to the literature.²⁵ The Raman signal of pyridine becomes extremely weak and almost unable to be detected as the potential shifts to more positive values, and the intensity of the 546 cm^{-1} band increases accordingly, indicating the increase in the concentration of surface oxides.

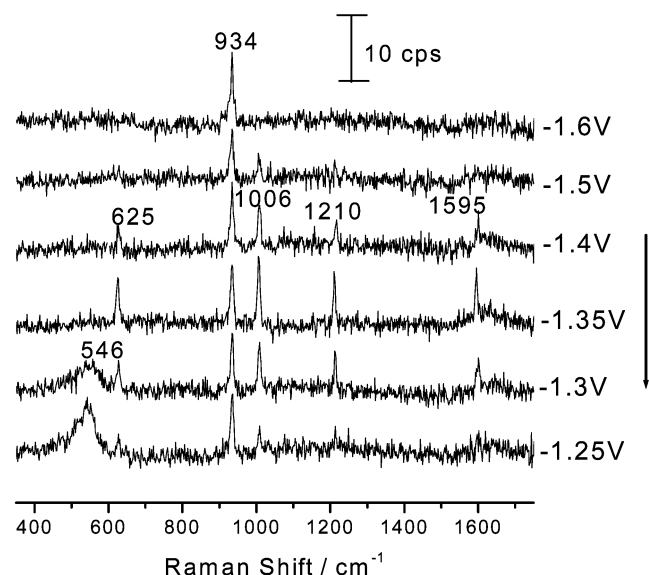
To our knowledge, there is no report to date on the interaction of pyridine and a zinc electrode using Raman spectroscopy. In comparison with the SERS from other transition metal surfaces, one can find some interesting points: a Zn electrode has a very narrow electrochemical window for observing the SERS. This property is closely related to the electrochemical behavior of Zn electrodes, where hydrogen evolution occurs easily on the surface while surface oxidation happens at slightly positive potentials. Second, the Raman signal of pyridine at the

roughened Zn electrode is much weaker than that at other transition metals, and the ν_1 frequency (1006 cm^{-1}) is lower compared to that of Pt (1010 cm^{-1}) and is very close to the value (1002 cm^{-1}) of solution-free species. This indicates that pyridine has a weaker interaction with Zn in comparison with coinage and Pt group metals. The difference may come from the inherent electronic structure of Zn. It is well known that the 3d and 4s orbitals of zinc are filled with electrons and there is no empty d orbital to accept electrons, which is different from coinage and transition metals. Therefore, zinc is inclined to be an electron donor, which is not beneficial for it to interact with pyridine.

The surface enhancement factor (SEF) for various roughened electrodes such as Pt, Rh, Fe, Co, Ni, etc. with different pretreatments have been calculated by using the unique calculation method based on a confocal Raman system.²⁶ For our experimental condition, the SEF for a roughened Zn electrode can be expressed as $G = 50CN_A\sigma I_{\text{surf}}/RI_{\text{bulk}}$. In this equation, C is the concentration of pyridine in solution, N_A is Avogadro's number, R is the roughness factor, σ is the area of a single

TABLE 1: List of G Values and Related Parameters for a Roughened Zn Electrode with Two Different Treatments

electrochemical roughening procedures	C ($\mu\text{F}\cdot\text{cm}^{-2}$)	R	I_{surf}	G (σ : 0.254 nm ²)	G (σ : 0.218 nm ²)
linear sweep ORC	90.8	1.9	71.7	257	221
A double step ORC	100.9	2.2	69.8	217	186

**Figure 4.** Potential-dependent SERS spectra of the adsorbed pyridine from a Zn electrode roughened by the linear sweep ORC method in 0.01 M pyridine + 0.1 M NaClO₄. The laser excitation line was 632.8 nm. Acquisition time: 20 s.

pyridine molecule adsorbed on the surface (pyridine is assumed to adsorb vertically), I_{surf} is the Raman signal of adsorbed pyridine on the surface, and I_{bulk} is that of free pyridine in the bulk solution. The roughness factor (R) is defined as a ratio of the real area of a roughened surface to that of a smooth surface. Analogous to Fe, Co, and Ni, we also used the electrochemical differential capacitance method to determine the R value of the roughened Zn electrode.^{27,28} On the basis of our experimental data, we estimate the enhancement factors to be about two orders of magnitude for pyridine on roughened Zn electrodes, which is close to the results from transition metals. The detailed results are listed in Table 1.

4. Conclusion

Two electrochemical roughening procedures have been found for obtaining SERS from bare Zn electrode. Potential dependent surface-enhanced Raman spectra of pyridine adsorbed on roughened Zn electrode have been obtained for the first time with a confocal Raman microscope. The surface enhancement factor has been calculated to be about two orders of magnitude. The relative weak Raman signal compared to other transition metal surfaces may be due to the weak electronic interaction between zinc and pyridine. Further experimental and theoretical work may be required for a better understanding of the SERS

mechanism of roughened Zn electrode; however, this study points to the very promising future of using the SERS of Zn electrode for understanding the physical chemistry processes occurring on zinc in some very interesting and important practical systems.

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References and Notes

- (1) McLarnon, F. R.; Cairns, E. J. *J. Electrochem. Soc.* **1991**, *138*, 645.
- (2) Deiss, E.; Holzer, F.; Haas, O. *Electrochim. Acta* **2002**, *47*, 3995.
- (3) Karpinski, A. P.; Makovetski, B.; Russell, S. J.; Serenyi, J. R.; Williams, D. C. *J. Power Sources* **1999**, *80*, 53.
- (4) Ghaemi, M.; Amrollahi, R.; Ataherian, F.; Kassaei, M. Z. *J. Power Sources* **2003**, *117*, 233.
- (5) Manov, S.; Lamazouere, A. M.; Aries, L. *Corros. Sci.* **2000**, *42*, 1235.
- (6) Aramaki, K. *Corros. Sci.* **2001**, *43*, 1985.
- (7) Ohtsuka, T.; Matsuda, M. *Corrosion* **2003**, *59*, 407.
- (8) Hugot-Le Goff, A.; Joiret, S.; Saidani, B.; Wiart, R. *J. Electroanal. Chem.* **1989**, *263*, 127.
- (9) Cai, M.; Park, S.-M. *J. Electrochem. Soc.* **1996**, *143*, 2125.
- (10) Zou, S.; Williams, C. T.; Chen, E.; Weaver, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 3811.
- (11) Zou, S.; Williams, C. T.; Chen, E.; Weaver, M. J. *J. Phys. Chem. B* **1998**, *102*, 9039.
- (12) Rubim, J.; Dönnwald, J. *J. Electroanal. Chem.* **1989**, *258*, 327.
- (13) Gui, J.; Devine, T. M. *J. Electrochem. Soc.* **1991**, *138*, 1376.
- (14) Tian, Z. Q.; Ren, B.; Wu, D. Y. *J. Phys. Chem. B* **2002**, *106*, 9464.
- (15) Loo, B. H. *J. Chem. Phys.* **1981**, *75*, 5955.
- (16) Brolo, A. G.; Odziemkowski, M.; Irish, D. E. *J. Raman Spectrosc.* **1988**, *29*, 713.
- (17) Fleischmann, M.; Tian, Z. Q.; Li, L. J. *J. Electroanal. Chem.* **1987**, *217*, 397.
- (18) Cai, W. B.; Scherson, D. A. *J. Electrochem. Soc.* **2003**, *150*, B217.
- (19) Tian, Z. Q.; Ren, B.; Mao, B. W. *J. Phys. Chem. B* **1997**, *101*, 1338.
- (20) Cai, W. B.; Ren, B.; Li, X. Q.; She, C. X.; Liu, F. M.; Cai, X. W.; Tian, Z. Q. *Surf. Sci.* **1998**, *406*, 9.
- (21) Cao, P. G.; Yao, J. L.; Ren, B.; Gu, R. A.; Tian, Z. Q. *Chem. Phys. Lett.* **2000**, *316*, 1.
- (22) Wu, D. Y.; Xie, Y.; Ren, B.; Yan, J. W.; Mao, B. W.; Tian, Z. Q. *PhysChemComm* **2001**, *18*, 1.
- (23) Huang, Q. J.; Yao, J. L.; Gu, R. A.; Tian, Z. Q. *Chem. Phys. Lett.* **1997**, *271*, 101.
- (24) Hassan, Hamdy H. *Appl. Surf. Sci.* **2001**, *174*, 201.
- (25) Damen, T. C.; Porto, S. P. S.; Tell, B. *Phys. Rev.* **1966**, *142*, 142.
- (26) Ren, B. Ph. D. Thesis, Xiamen University, China, 1998, p 74.
- (27) Trasatti, S.; Petrii, O. A. *Pure Appl. Chem.* **1991**, *631*, 711.
- (28) Brown, D. S.; Farr, J. P. G.; et al. *J. Electroanal. Chem.* **1968**, *17*, 421.