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# Electrochemically Roughened Palladium Electrodes for Surface-Enhanced Raman Spectroscopy: Methodology, Mechanism, and Application

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Palladium is one of the important materials in surface sciences due to its unique catalytic activities toward various reactions. To study the process occurring on the palladium surface by Raman spectroscopy, it is necessary to obtain a surface with surface-enhanced Raman scattering (SERS) activity. We reported here the preparation method for obtaining SERS-active pure massive palladium electrodes via an electrochemical roughening method by strictly controlling the roughening potential and frequency. The roughened surface consists mostly of spherical nanoparticles with a diameter of 50–60 nm. The SERS activity of the electrode was demonstrated by using pyridine as a model molecule, and it was found that the surface enhancement could be as high as 3 orders of magnitude. With such high enhancement, we were able to study processes related to molecules with small Raman cross sections, such as CO. Distinctly different from other transition metals in the VIIIIB group, palladium electrode shows SERS activity clearly dependent on the wavelength of the excitation laser, with highest enhancement appearing at 632.8 nm. To understand the enhancement mechanism, a finite difference time domain method was used to simulate the optical properties of the roughened palladium surface, and it was found that electromagnetic enhancement plays an important role in the SERS of the palladium, which is in good agreement with the experimental result.

## 1. Introduction

Palladium is a metal of high catalytic activity, which leads to its important applications. The ability to absorb 800–900 times its own volume of hydrogen at room temperature and atmospheric pressure leads to several integral roles of palladium in a hydrogen economy.<sup>1,2</sup> It can be used to generate, purify, store and detect hydrogen and becomes an important material for fuel cell technology.<sup>3</sup> There are also numerous studies underway to pioneer techniques to use palladium as a catalyst.<sup>4–6</sup> For example, it has been used to promote the chemical conversion of contaminants (such as trichloroethylene and tetrachloroethylene in groundwater) into benign end products in the presence of added hydrogen gas to replace the chlorine atoms in the contaminant with hydrogen.<sup>4</sup> Palladium has also been used as a heterogeneous catalyst for reduction of car exhausts (due to high catalytic activity for NO reduction) to reduce air pollution.<sup>5</sup> In electrochemistry, it is an important metal used for oxygen reduction, nitrite reduction, etc.<sup>6</sup> However, there are still a lot of mechanistic problems existing, for which vibrational spectroscopy may provide helpful information.

Among the various vibrational spectroscopies, Raman spectroscopy is a very promising one, especially in electrochemical environments. However, as pointed out in our previous studies, the surface-enhanced Raman scattering (SERS) of transition metal surfaces are relatively weak compared to coinage metals, and the number of metal that can provide SERS are still limited.<sup>7</sup> After several years of systematic studies, we have been able to extend SERS to metals other than Au, Ag, and Cu, including massive transition metals, Fe, Co, Ni, Pt, and Rh and electrodeposited Ru and Pd surfaces.<sup>8–13</sup>

Due to the above-mentioned importance of Pd to surface sciences, there are increasing investigations on obtaining SERS from this metal. As early as 1982, Loo<sup>14</sup> pointed out that due to the lack of appropriate bonding orbitals in Pd with pyridine, the interaction between them is very weak, which led to an undetectable SERS signal of pyridine on Pd. The first reported surface signal on Pd dates back to 1983, when Fleischmann et al.<sup>15</sup> obtained a signal for pyridine on  $\beta$  Pd–H electrode. However, the necessity for CO to be present during the oxidation and reduction cycles (ORC) for obtaining SERS of pyridine indicates that what they obtained is a kind of surface complex formed by Pd, CO, and pyridine rather than adsorbed pyridine. They have not reported any result from pure Pd electrode surfaces.

The most important development in the SERS of Pd was brought about with the fast development of nanoscience and nanotechnology. In recent years, there have been increasing reports on chemical methods to obtain Pd nanoparticles of various sizes and shapes, used as SERS substrates. In 1997, Vlčková and co-workers<sup>16</sup> obtained for the first time a SERS signal of 4,4'-bipyridine in Pd sols; the enhancement is estimated to be about 190.<sup>16</sup> Seven years later, Gómez et al.<sup>17</sup> obtained a Pd SERS substrate by dispersing chemically synthesized Pd nanospheres on a glassy carbon surface and revealed an enhancement of ca. 550 for the adsorbed CN<sup>−</sup>. Xia and co-workers<sup>18</sup> synthesized a series of Pd nanoparticles, varying from nanocubes to nanoboxes to nanocages, and revealed enhancements about 2–4 orders of magnitude for the adsorbed 4-mercaptopyridine depending on the shape and size of the nanoparticles, with the maximum enhancement obtained on Pd nanoboxes. The high enhancement allows them to detect 4-mercaptopyridine with concentrations as low as nanomolar. Another study reveals that triangular and hexagonal nanoparticles give even higher

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enhancement.<sup>19</sup> However, it should be pointed out that the capping agent or surfactants used in the wet chemical preparation of nanoparticles will limit to some extent the application of this kind of SERS substrate, because these agents stay at the very first layer of the nanoparticles and will prevent the adsorption of some molecules with weak interaction with Pd electrodes.<sup>16–19</sup> Therefore, along with the great success of nanoparticle-based SERS substrates, it is still meaningful to explore other means for preparing Pd SERS substrates.

As early as 1987, Weaver and co-workers<sup>20–22</sup> started to coat Pd over SERS-active Au substrate to obtain SERS from a Pd electrode, and the method has been used quite successfully in some systems. However, the difficulty of eliminating completely the pinhole is a very challenging issue in this method. In 2002, Weaver and co-workers<sup>23</sup> proposed a method to prepare Pd-coated Au nanoparticle thin films over ITO surfaces by chemical replacement of UPD-deposited Cu layer on Au with Pd, which allowed them to obtain pinhole-free Pd layers. However, there has been no continuous work along this direction after the sudden passing away of Weaver. As hinted from this method, our group, on the other hand, used a seed-growth method to directly obtain pinhole-free Pd shell Au core nanoparticles.<sup>24,25</sup> However, the impurities originating from the preparation procedures of the nanoparticles and the stability of the thin Pd film still limit to some extent a wide application of the method. It should be pointed out that the standpoint of thin film or core–shell method is to use the enhancement from Au underneath the Pd layer rather than Pd itself. Therefore, it is impossible for this method to answer whether Pd itself is SERS-active and thereby to explore the SERS mechanism of Pd.

In 1997, our group obtained the first SER spectrum of pyridine from electrodeposited Pd electrodes.<sup>13</sup> However, the signal is relatively weak, which is essentially unsuitable for detailed study of some practical systems. On the basis of the background just described, in this paper, we propose an electrochemical roughening method to obtain SERS-active pure massive Pd electrodes by using 1 M H<sub>2</sub>SO<sub>4</sub> solution as the roughening solution. The Pd electrode thus prepared gave enhancement as high as 3 orders of magnitude for pyridine and free of impurities, which allows us to discuss the SERS mechanism of Pd. Most interestingly and importantly, we have found for the first time that the SERS of Pd shows very characteristic dependence on the excitation wavelength, which has not been found on all other transition-metal surfaces. A very preliminary theoretical calculation was made to understand the mechanism.

## 2. Experimental Section

SERS measurements with 632.8 nm excitation were performed with a LabRam I confocal microscope Raman system (Horiba/JY, France). The microscope objective for laser illumination and signal collection was of long working distance (8 mm) with 50× magnification and a numerical aperture of 0.55. The excitation line was from an air-cooled He–Ne laser, and the laser power was about 7 mW on the sample.

SERS measurements with 514.5 and 785 nm excitation were performed with a Renishaw R-1000 UV–visible confocal microprobe Raman system. The microscope objective for laser illumination and signal collection was of long working distance (8 mm) with 50× magnification and a numerical aperture of 0.55. The excitation line of 514.5 nm was from an air-cooled Ar<sup>+</sup> laser and that of 785 nm was from a diode laser. The laser power was about 7 mW on the sample.

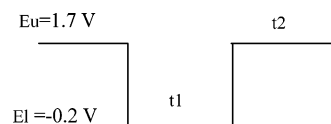


Figure 1. Square waveform for roughening the Pd electrode.

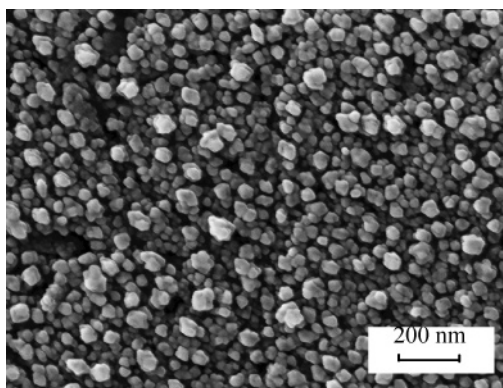
The working electrode was made from a polycrystalline Pd rod of 99.9% purity from Alfa Aesar. To obtain a Pd electrode with high purity and good electrochemical response, the rod was first melted in a hydrogen flame into a bead for over 2 min so that part of the impurities will be concentrated on the surface, which is called zone melting and refining. Then, the bead was dipped into aqua regia to dissolve impurities concentrated on the surface, followed by cleaning with Milli-Q water. After several cycles of melting and dissolution, the bead was sealed into a Teflon shroud while being heated. The obtained electrode should then be polished to a mirror finish. The geometric area of the surface is about 0.03 cm<sup>2</sup>.

A large platinum ring served as the counterelectrode. The reference electrode was a saturated calomel electrode (SCE); thus all the potentials in this work are quoted versus SCE. The applied potential during the electrochemical roughening and cyclic voltammograms were recorded on a CHI631A electrochemical workstation (CH Instruments). The electrode potential during the Raman measurements was controlled by an XD-II potentiostat (Xiamen University). Scanning electron micrographs (SEM) were obtained on LEO1530 operated at 20 kV.

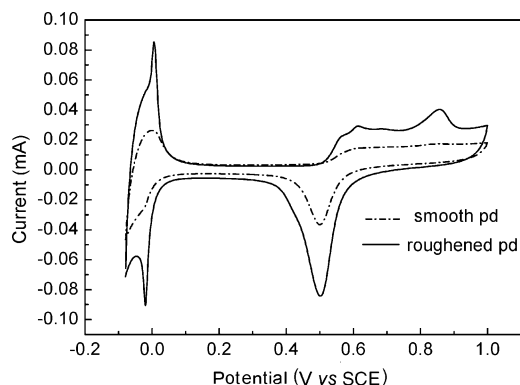
## 3. Results and Discussion

Besides the wet chemical method for preparing colloidal metal nanoparticles, the electrochemical method is also one of the most important methods to obtain SERS-active substrates. Although Pd is in the Pt-group metals, the very top layer of atoms can be easily oxidized in air. By applying an oxidation potential to the Pd electrode in an electrochemical environment, a compact oxide layer can be easily formed on the Pd surface, leading to a surface showing black color, which prevents further oxidation of the electrode. Therefore, it is difficult to obtain a Pd electrode with large surface area by simply applying an oxidation potential. In the 1980s, Arvia and co-workers<sup>26</sup> developed a method that allows them to obtain Pt-group metals with large surface area. The method is termed potential reversal technique<sup>27</sup> and can easily produce a Pd electrode with very large surface area.<sup>28</sup> We adopted the same condition as that used by Arvia, and it is true that we could obtain a Pd electrode with large surface area. However, the Pd surface showed only a very weak SERS effect. A similar result has been obtained in our previous study of Pt electrodes, and we found that the surface enhancement is not proportional to the surface area. There is an optimal surface roughness, beyond which the surface enhancement will decrease with increasing surface area.<sup>29</sup>

Hinted from the roughening procedure of Pt electrodes and the experience in obtaining SERS in Pt systems, we carried out a systematic study by changing the potential range (oxidation and reduction potential values) as well as the frequency used, and we obtained Pd electrodes with reasonably good SERS activity. The detailed electrochemical roughening parameters are shown in Figure 1. The roughening solution is 1 M H<sub>2</sub>SO<sub>4</sub>. Before roughening, the smooth Pd electrode should first be electrochemically cleaned in the above solution by potential cycling between −0.2 and 1.2 V at a rate of 0.5 V/s until reproducible cyclic voltammograms are obtained, normally for about 1–2 min. Then a symmetric square-wave potential was



**Figure 2.** SEM image of the roughened Pd electrode.

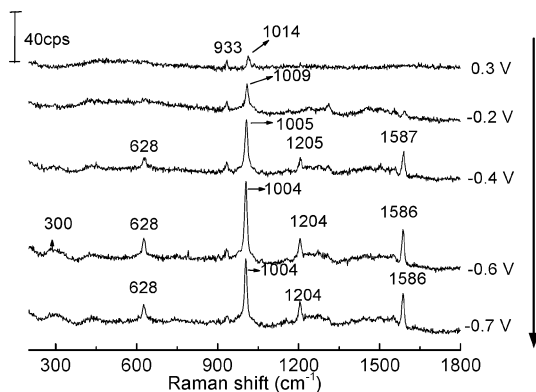


**Figure 3.** Cyclic voltammograms of smooth (---) and roughened Pd (—) in 1 M H<sub>2</sub>SO<sub>4</sub>. Scan rate 50 mV/s.

applied to the Pd electrode for ca. 20–30 s, with oxidation potential of 1.7 V, reduction potential of −0.4 V, and frequency of 600 Hz. Afterward, the electrode was held at −0.1 V for about 350 s for a complete reduction of the surface oxides formed. It should be pointed out that Pt-group metals, after such treatment, show very high catalytic activity. Therefore, before being used for Raman measurement, the electrode should generally be cycled again in the same solution to remove some very active surface sites (a procedure called electrochemical stabilization) under the same conditions as for the electrochemical cleaning.

The roughened Pd electrode surface presents a very uniform appearance as observed with naked eyes and microscope. Unlike the gray or dark brown color observed in other roughened Pt-group metals, the Pd surface shows a bluish color, indicating a unique optical property of the Pd surface. A typical SEM image of the roughened Pd electrode is shown in Figure 2, which shows nanoparticles with diameters from 30 to 60 nm, with average size of 50 nm. Likewise, the Pd is dissolved during the oxidation process and redeposited as nanoparticles on the surface.

To characterize the electrochemical properties of this type of electrode, cyclic voltammetric studies were carried out. Figure 3 gives cyclic voltammograms obtained from smooth and electrochemically roughened Pd in 1 M H<sub>2</sub>SO<sub>4</sub> at a scan rate of 50 mV/s over the potential range from −0.1 to 1 V. The smooth Pd electrode shows electrochemical features very similar to those reported in the literature.<sup>28</sup> The roughened Pd electrode presents essentially the same features as the smooth electrode except that the roughened Pd gives better-resolved hydrogen adsorption and desorption peaks in the negative potential region. Different behavior in the hydrogen region has also been observed in a recent study of nanostructured Pd layers, which is closely related to the properties of nanoparticles.<sup>6</sup> The surface area of a Pd electrode can be estimated by integration of the charge for the



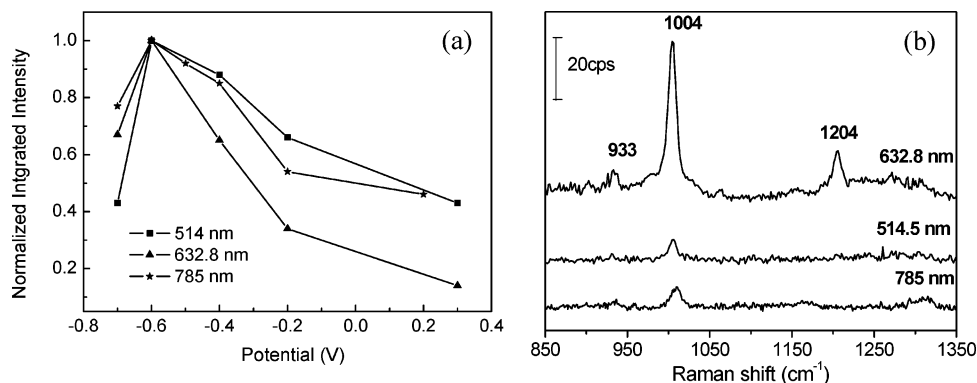
**Figure 4.** Potential-dependent SERS of pyridine on a roughened Pd electrode in 0.01 M pyridine + 0.1 M NaClO<sub>4</sub>. Excitation line 632.8 nm; acquisition time 60 s.

electrochemical reduction of Pd oxides, appearing at ca. 0.5 V. Hence the surface roughness factor  $R = Q_r/Q_s$ , where  $Q_r$  and  $Q_s$  are the areas of the electroreduction peak for roughened and ideally smooth Pd electrodes (with a value of 424  $\mu\text{C}/\text{cm}^2$ ).<sup>30</sup> The  $R$  value is very important for estimating the surface enhancement effect, and in the case of Pd electrode we can obtain  $R$  values in the range of 5–8 depending on roughening time and geometric area of the electrode.

To demonstrate the SERS activity of the roughened Pd surface, we selected pyridine, a molecule with a relatively large Raman cross-section, as the probe molecule, as in our previous studies of other transition metals.<sup>8–13</sup> The SERS spectra were acquired on the roughened Pd electrode surface immersed in 0.01 M pyridine + 0.1 M NaClO<sub>4</sub> solution under potential control and are shown in Figure 4. The spectra were collected stepwise from positive toward negative potentials, starting from the open circuit potential. From the figure we can find four strong bands located at 628, 1005, 1205, and 1587  $\text{cm}^{-1}$ , which are all the characteristic peaks related to adsorbed pyridine.<sup>31</sup> The band at ca. 933  $\text{cm}^{-1}$  is due to the symmetric stretching vibration of ClO<sub>4</sub><sup>−</sup> in the solution. As can be seen from the figure, the intensity of the bands related to adsorbed pyridine shows a clear potential dependence. The SERS signal of pyridine is very weak at the open circuit potential and increases with the negative movement of the electrode potential, with the maximum intensity appearing at −0.6 V. Further negative movement of the electrode potential results in a decrease of the SERS intensity. Besides the intensity change, the frequencies of some peaks also change with potential, especially the peak at 1005  $\text{cm}^{-1}$  related to the  $a_1$  ring breathing mode. The dependence of both the intensities and frequencies on the applied potential indicates the signal is from surface species. In the potential region from 0.3 to −0.2 V, there is a broad feature in the frequency region from 300 to 700  $\text{cm}^{-1}$ , which may come from the surface oxides, that prevents the adsorption of pyridine on the pure Pd surface and leads to a significant difference in the frequency and intensity of the adsorbed pyridine. In the potential region between −0.4 and −0.7 V, we observed a band at ca. 300  $\text{cm}^{-1}$ , which may come from the Pd–N vibration according to our previous study of Pt and other transition metal systems.<sup>8–13</sup> It would indicate that the pyridine is bound through its N atom to the surface.

The stability of a SERS substrate is crucially important to its application. It has been found that the SERS activity of a traditional SERS substrate, Ag, will be significantly decreased or even irreversibly quenched upon a short excursion at negative potentials. Such irreversibility of the substrate itself may bring extra difficulty to explain the experimental finding or even lead





**Figure 5.** (a) Profile of normalized integrated intensity of the ring breathing vibration band of pyridine as a function of the potential on a roughened Pd electrode in  $10^{-2}$  M pyridine + 0.1 M NaClO<sub>4</sub>. (b) Excitation wavelength-dependent SER spectra for pyridine adsorbed on the roughened Pd electrode.

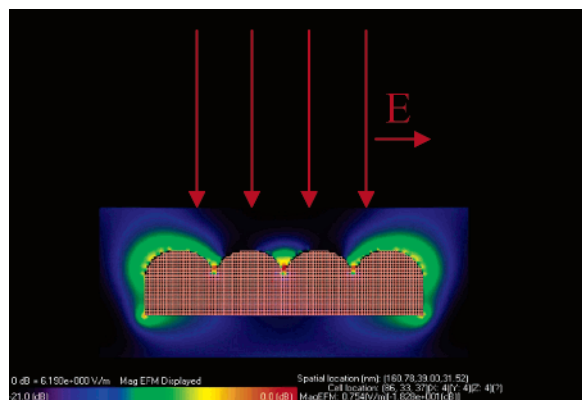
to a misinterpretation of the experimental results. We have pointed out in the Introduction that the SERS substrates prepared by pure metal nanoparticles or core-shell metal nanoparticles may suffer from the problem of impurities and the stability of the nanoparticles in some specific application. On the other hand, the Pd electrode surface prepared by electrochemical roughening shows comparatively good stability. For example, as in the case of Figure 4, if we turned the potential from  $-0.7$  V back to positive values and then changed the potential back to  $-0.6$  V, we found only 10% decrease in the total SERS signal, indicating that the Pd surface has a relatively good SERS reversibility. However, we found that one has to be very careful about the negative extremity of the potential. If the potential is changed into the hydrogen absorption region, the absorbed hydrogen will totally change the properties of the Pd electrode, which will lead to a significant decrease of the SERS activity. It should be pointed out that, due to the relatively active chemical properties of Pd, the SERS reversibility will not be as good as that of Pt and Rh; however, it is much better compared with Fe, Co, and Ni and even better than Ag.

As mentioned above, the observed Raman signal in Figure 4 is from the surface-enhanced Raman signal of adsorbed pyridine. Then, one may naturally wonder how much is the enhancement effect of such a surface? For this purpose, we estimated the surface enhancement factor of the Pd electrodes according to the method proposed in ref 29,  $G = (I_{\text{surf}}/N_{\text{surf}})/(I_{\text{bulk}}/N_{\text{bulk}})$ , which can be rearranged as  $G = (cN_A\sigma h I_{\text{surf}})/(R I_{\text{bulk}})$ , where  $c$  is the concentration of adsorbate (0.1 M) and  $N_A$  is the Avogadro constant ( $6.02 \times 10^{23}$ ).  $\sigma$  is an empirical value of the surface area occupied by each pyridine molecule, which is about  $0.254 \text{ nm}^2$ .<sup>29</sup>  $h$  is an experimental value characterizing the confocal quality of the microscope Raman system, which is  $60 \mu\text{m}$ .  $R$  is the surface roughness of the Pd electrode, which is 6 in the present case.  $I_{\text{surf}}$  and  $I_{\text{bulk}}$  are the experimental values of the integrated intensity for pyridine adsorbed on the surface and in the aqueous solution, which are 679 and 54 counts/s, respectively. On the basis of these data,  $G$  is estimated to be about  $1.8 \times 10^3$ . This value is indeed comparable with the maximum enhancement in the case of Pt<sup>11</sup> but slightly lower than that of Rh.<sup>12</sup> However, this value shows similar enhancement to the electrode assembled by Au@Pd core-shell nanoparticles with a thick Pd shell, indicating that in the case of thick layer of Pd the contribution of the Au core can be negligible.<sup>24,25</sup> This enhancement is obviously stronger than pyridine on a Pd film electrochemically deposited on a glassy carbon electrode.<sup>13</sup>

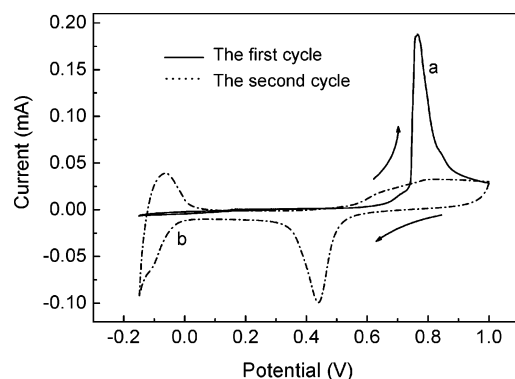
Then, why can we obtain the surface enhancement from Pd electrode, and what is the enhancement mechanism? For this

purpose, we changed the excitation wavelength and investigated the dependence of the surface-enhanced Raman signal on the excitation wavelength. For clarity, we plotted the SERS intensity with the potential for each excitation line, and the result is shown in Figure 5. Surprisingly, the signals obtained with both the 514.5 and 785 nm excitation are very weak compared with that obtained with 632.8 nm excitation. Over the investigated potential range, we did not observe a shift in the potentials of maximum intensity with the excitation wavelength. However, the involvement of the hydrogen absorption at potentials negative of  $-0.7$  V, which will lead to a decrease in the SERS activity of Pd, makes the determination of potential of maximum intensity difficult. Therefore, on the basis of only the present result, it is still not sufficient to exclude totally the charge-transfer effect. However, one may assume the charge-transfer effect is not very significant. Then, what leads to the significant difference in the SERS activity at different wavelengths? Such wavelength-dependent behavior has not been observed in any other transition metals that have been investigated in our group, including Pt, Rh, Fe, Co, and Ni,<sup>8-13</sup> which can be reasonably understood because surface plasmon resonance is generally not operative on these metals. However, Pd appears to be an exception. We have tried to do UV-vis absorption on the Pd surface; however, due to the very small size of the electrode, the strong background in the reflection mode, and the difficulty of finding a suitable reference, the attempt was unsuccessful. Although a strict experiment in this aspect will be very helpful for understanding the behavior, we can still reason that surface plasmon resonance may play an important role in the SERS of Pd. As has been pointed out previously, the roughened Pd electrode presents a bluish color, which may indicate that the surface has a characteristic absorption at a certain wavelength, most probably in the red (complementary to blue). Such a characteristic color indicates the possible involvement of surface plasmon resonance of the nanostructures on the Pd surface. It should be especially pointed out that such wavelength-dependent SERS activity has not been reported on Pd nanoparticle systems or thin Pd films. Although Xia and co-workers<sup>18</sup> reported the absorption of Pd nanoparticles in the green region, their experiments were carried out with only near-infrared laser excitation, which is out of the resonance of absorption. Gómez et al.<sup>17</sup> used the same laser line as us. However, they did not report any result excited with other wavelengths. Therefore, it is still worthwhile to carry out systematic study on Pd systems of various structures.

To further understand the mechanism, we carried out a three-dimensional finite difference domain time (FDTD) calculation of the enhancement effect of the roughened Pd surfaces.



**Figure 6.** Three-dimensional FDTD simulation of the electromagnetic field enhancement of four Pd nanoparticles connected successively. Incident laser wavelength 632.8 nm.



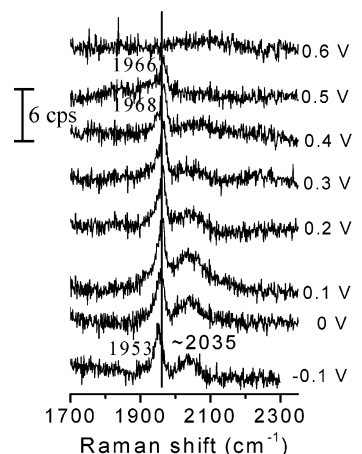
**Figure 7.** Cyclic voltammograms of oxidation of CO adsorbed on a roughened Pd electrode in 0.1 M  $\text{H}_2\text{SO}_4$ : (a) first cycle (—); (b) second cycle (---). Scan rate 50 mV/s.

According to the SEM result, we used Pd hemispherical nanoparticles with a diameter of 50 nm connected to a Pd plate to simulate the roughened Pd surface. The laser was irradiated perpendicularly to the surface plane, with the electric field vector along the diagonal axis of the four particles, as indicated in Figure 6. The yee cell size was  $0.5 \text{ nm} \times 0.5 \text{ nm} \times 0.5 \text{ nm}$ , and the total number of time steps was 15 000 to ensure the convergence.

The model and the calculated field distribution surrounding the surface are shown in Figure 6. From Figure 6, we can find that the maximum field enhancement occurs in the interstices between nanoparticles, with a value of 6.19. This value amounts to 1470-fold enhancement in SERS. When the enhancement is averaged over the whole surface, the enhancement may be smaller. Even so, this value is still in good agreement with the experimentally observed enhancement, indicating the importance of electromagnetic effect in the SERS of Pd.

Success in obtaining a SERS signal from pyridine on pure Pd electrode surface with very good signal-to-noise ratio encourages us to investigate systems of very small Raman cross section but with great practical significance. As mentioned in the Introduction, Pd and its alloys have been widely used in fuel cells and electrocatalytic systems. In methanol fuel cells, CO has been considered as one of the main poisoning intermediates produced by the dissociation of C1 molecules on Pt-group metals. Therefore, it is worthwhile to investigate CO adsorption and oxidation on the Pd electrode surface.

Figure 7 shows the first two cycles of the cyclic voltammograms of a roughened Pd electrode in 0.1 M  $\text{H}_2\text{SO}_4$  solution with a saturated monolayer of CO. To ensure saturated adsorption of CO on the surface, the Pd electrode was immersed in



**Figure 8.** Representative potential-dependent SERS spectra for saturated CO on the roughened Pd electrode in 0.1 M  $\text{H}_2\text{SO}_4$ .

0.1 M  $\text{H}_2\text{SO}_4$  saturated with CO with the potential controlled at  $-0.1 \text{ V}$  for 30 min and then  $\text{N}_2$  was purged for 10 min to remove the dissolved CO for the cyclic voltammogram measurements.

As can be seen from the figure, in the first cycle, the current related to hydrogen adsorption or absorption is almost completely suppressed due to the existence of CO. An anodic peak initiating at ca. 0.55 V and reaching a maximum at 0.78 V is related to the oxidation of adsorbed CO layer on Pd. After removal of CO from the surface, the surface returned to the character of a clean Pd surface with the reappearance of a reduction peak of Pd oxides and the adsorption and desorption of hydrogen. In comparison with Pt or Rh, CO was oxidized at a more positive potential, indicating a very strong interaction between Pd and CO or lower catalytic activity of Pd toward the oxidation of CO. However, it can be inferred from the result that one potential cycle is sufficient to oxidize almost all CO adsorbed on the roughened Pd surface.

A SERS study of CO adsorption on Pd was carried out with the characteristic potentials obtained in the above electrochemical study. Figure 8 shows the potential-dependent SERS spectral sequences for a saturated CO layer on the roughened Pd in 0.1 M  $\text{H}_2\text{SO}_4$ . Two bands in the high-frequency region, located at ca. 2035 and ca. 1953–1968  $\text{cm}^{-1}$ , can be observed, which can be related to the C–O vibrations of linearly bonded and bridge-bonded CO, respectively. The frequency of the bridge-bonded CO blue-shifts with the positive movement of the electrode potential with a slope of  $30 \text{ cm}^{-1}/\text{V}$ , due to the electrochemical Stark effect.<sup>17,22</sup> The intensities of both bands increase first and then decrease with the positive movement of the electrode potential, with the maximum intensity appearing at 0.1 V. The SERS signal decreases significantly at 0.5 V, just before the initial potential of CO oxidation, and then becomes totally undetectable. The different phenomena observed with cyclic voltammetry and SERS are due to the fact that the former is a transient technique whereas SERS was performed under static conditions.

It can be seen from Figure 8 that the bridge-bonded CO shows higher SERS intensity (both integrated and peak intensity) compared with the linearly bonded species, which is very different from that on Pt<sup>11</sup> and Rh,<sup>32</sup> indicating that the bridge-bonded species is dominant at the Pd surface. The percentage of bridge-bonded CO on the metal surfaces decreases in the order  $\text{Pd} > \text{Rh} > \text{Pt}$ . It is interesting to compare the present result with that reported in the literature. Up to now, there have

been two SERS reports on CO adsorbed on Pd surfaces.<sup>17,22</sup> In the SERS study of Zou and Weaver,<sup>22</sup> it was found that the bridge-bonded and linearly bonded CO appeared at 1963 and 2060  $\text{cm}^{-1}$  respectively, on the Pd-coated Au substrate. On a Pd nanoparticle surface, Gómez et al.<sup>17</sup> observed the two species at ca. 1965 and 2091  $\text{cm}^{-1}$ . Our result shows a similar frequency to the SERS results of Weaver and Gómez as well as the infrared result of Pd single-crystal surface for the bridge-bonded species. The potential-dependent behavior almost dictates the IR result on Pd(110).<sup>33</sup> However, a significant difference was found in the frequency for the linearly bonded species, which is at ca. 2091, 2060, and 2035  $\text{cm}^{-1}$  on Pd nanoparticles, Pd-coated Au surface, and pure Pd surface, respectively, although the experiments were all done at saturated CO adsorption. This difference may be due to the intrinsic differences in surface structure between the nanoparticle surface, the thin film surface, and the pure Pd surface. Apparently, more experiments are necessary in order to totally understand the substrate effect on CO adsorption.

### Concluding Remarks

By electrochemically roughening the massive Pd electrode surface, we have successfully obtained a SERS-active Pd electrode. The surface enhancement was estimated to be around 3 orders of magnitude. Due to the interference of hydrogen absorption, whether charge-transfer contributes the surface enhancement is not conclusive. However, the wavelength-dependent SERS intensity change reveals that electromagnetic enhancement plays an important role in the SERS of Pd. The FDTD calculation result based only on electromagnetic field enhancement reveals a surface enhancement consistent with the experimental value. With the high enhancement provided by the Pd electrode, the investigation of CO adsorption and oxidation on the Pd surface was carried out, and the result indicates that CO is very sensitive to the surface states of electrode. The present study demonstrates that it is practical to use Pd as a SERS substrate for investigating systems of both fundamental and application interest. Further extension of the Pd electrode system may be to explore some interesting systems, such as hydrogen adsorption,  $\text{NO}_2$  reduction, and oxidation of small organic molecules.

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