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Kinetic Features of SERS Quenching by Underpotential Deposition (UPD) of Cd and Tl on Ag Electrodes

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Surface-enhanced Raman scattering (SERS) in the Ag/pyridine system is quenched through a biphasic kinetics, after completion of submonolayer underpotential deposition (UPD) of Cd. This result is elucidated by invoking a quasi-reversible transformation of the initial SERS-active site into another by an attack, *via* surface diffusion, of deposited Cd, followed by irreversible unimolecular decomposition of the new site. From the SERS quenching data a value of about 10^{-17} cm^2 s^{-1} was derived as the surface diffusion coefficient of Cd on the Ag surface. A similar but somewhat different quenching behavior is observed by UPD of Tl.

A number of authors[1–4] have recently described the use of underpotential deposition (UPD) of foreign metals onto Ag electrodes for mechanistic investigation of the surface-enhanced Raman scattering (SERS).[5] The SERS-quenching effect observed by UPD is generally very drastic, causing nearly perfect intensity loss at metal coverages on the order of several hundredths.[1–3] Moreover, the quenching effect is usually of irreversible nature, *i.e.*, the original SERS intensity is hardly recovered upon reoxidation (stripping) of the deposited foreign metal.[1–4] Such quenching behaviors have been accounted for by invoking an attack or association of the metal atom to some special "SERS-active site," which is supposed to exist on the Ag surface sustaining the SERS effect.

In a more recent work[6] we presented evidence that the SERS-active sites consist of sparingly soluble surface Ag$^+$ complexes, which are removed from the surface by the action of appropriate ligands forming water-soluble Ag$^+$ complexes, or are disintegrated through reduction of the Ag$^+$ centers by application of sufficiently negative potentials. Other workers[7,8] also identify the SERS-active sites with insoluble Ag$^+$ salts on the electrode surface. Then, as briefly discussed previously,[6] one of the possible mechanisms for the SERS-quenching by UPD may be related to an interaction between the deposited metal atom and the surface Ag$^+$ complexes. This aspect has been studied in the present work by following the time courses of the UPD itself and of the SERS intensity decrease.

Experimental

A polycrystalline Ag platelet (10×10×1 mm) embedded in a Teflon holder was used as a working electrode in a base electrolyte solution containing 0.1 M KCl and 0.05 M pyridine (1 M=1 mol dm^{-3}). CdCl$_2$ or TlCl was then dissolved to give a metal ion concentration of 2.5×10^{-5} M. The pH values of the Cd^{2+} and Tl$^+$ solutions were 8.5 and 7.7, respectively. No turbidity was noticed in the Cd^{2+}-containing solution, in contrast to a solution with much higher Cd^{2+} concentration (5×10^{-4} M).[4] The counter and reference electrodes are a Pt wire and a saturated calomel electrode (SCE), respectively.

Stripping voltammetry was used to determine the surface coverage $\theta(E,t)$ for Cd or Tl on tha Ag electrode as functions of potential E and polarization time t in the above-specified electrolyte solution. In this measurement a mirror-finished Ag electrode was employed, the roughness factor of which was estimated to be about 1.5 as in a previous work.[1] The stripping charge Q, corrected for the roughness factor, was converted to θ assuming θ=1 for Q=420 μC cm^{-2} (Cd) and 210 μC cm^{-2} (Tl).[9]

The pyridine SERS spectra were recorded over a wavenumber range of 985—1045 cm^{-1}, in which two major vibrational peaks are observed. A single scan required about 6 s. Other details for SERS measurements are the same as in a previous paper,[1] except that a 514.5-nm Ar$^+$ laser line (100 mW) was used here for excitation.

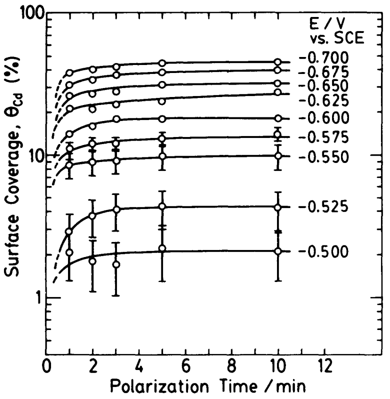

Fig. 1. Effect of electrode potential and polarization time on θ_{Cd} on the Ag electrode surface. [Cd^{2+}]= 2.5×10^{-5} M.

Results and Discussion

UPD of Cd. Figure 1 shows the $\theta_{Cd}(E,t)$ characteristics obtained with a mirror-finished Ag electrode. It is seen that measurable UPD starts at a potential *ca.* 300 mV positive of the thermodynamic deposition potential for the Cd^{2+}/Cd couple (−0.78 V *vs.* SCE at $[Cd^{2+}]=2.5\times10^{-5}$ M). No significant difference was noted between the features of $\theta_{Cd}(E,t)$ in the presence and absence of 0.05 M pyridine. A similar observation is described by Kester[4] for the θ_{Tl} values in the Ag/benzotriazole system. Further, the application of an oxidation-reduction cycle (ORC), leading to roughening of the Ag surface, did not alter the essential feature of $\theta_{Cd}(E,t)$, except for some fourfold increase in the stripping charge Q due to roughening. The most important aspect in Fig. 1 is that the UPD process is practically completed in less than 100 s at each potential. A closer examination of the temporal evolution of θ_{Cd} demonstrated that the effective times for near-completion of UPD were about 40 s and 120 s for Ag electrodes before and after an ORC, respectively.

The SERS quenching effect of Cd UPD was examined as follows. After application of an ORC to a reformation charge of about 20 mC cm^{-2} in an electrolyte solution containing all the three components (pyridine, KCl, and $CdCl_2$), the potential was maintained for 1—2 min at 0.0 V *vs.* SCE to achieve a stationary SERS signal. The potential was then stepped to a negative value, ranging from −0.45 to −0.7 V, and the SERS spectra were thereafter registered every 20 s for about 40 min. Potentials negative of −0.7 V were avoided because of the occurrence of potential-induced irreversible decay of the pyridine SERS.

In a Cd^{2+}-free electrolyte solution, the pyridine SERS intensity was stable for more than 40 min at potentials from 0.0 to −0.7 V. In the presence of 2.5×10^{-5} M Cd^{2+}, a drastic decay of the intensity was observed by stepping the potential to a range of −0.48 to −0.70 V, in correspondence with the occurrence of UPD. In the initial phase of the intensity decay, a change in the SERS spectrum was also noted. These results are summarized in Fig. 2. Here the intensity is represented by the peak height of the totally symmetric vibration at 1007 cm^{-1} (I_{1007}), and the spectral shape by the intensity ratio I_{1007}/I_{1037}. The following features are noticed in this figure: (1) The intensity decay occurs essentially after the completion of Cd UPD, which takes less than 120 s as mentioned above; (2) The intensity decay apparently obeys a biphasic kinetics, with the time constant of the first phase being dependent on the potential (and hence on the θ_{Cd} value), while that of the second phase being practically potential-independent; and (3) The shape of the pyridine SERS spectrum undergoes a change exclusively during the first phase of the decay, and remains nearly unchanged throughout the second phase. The pattern of the spectral change, namely the direction of the change in the peak height ratio, is seen to depend on the potential. Besides such a peak height ratio change, some peak wavenumber shift was also noted (*e.g.*, a shift from 1007 cm^{-1} to 1009 cm^{-1} at −0.7 V within the initial 500 s). A change in the SERS spectrum as well as in the intensity has also been observed by Kester,[4] regarding the quenching of SERS in an Ag/benzotriazole (BTA) system by UPD of Tl, and was ascribed to some unknown effect of deposited Tl on the Ag–BTA interaction.

These results indicate that the SERS quenching in the Ag/pyridine system by UPD of Cd consists in the attack of deposited Cd atom to the initial "SERS-active site (A)" to produce a new site B (which is still SERS-active), followed by a unimolecular decomposition of B into a SERS-inactive site, X. Denoting the time constants of these sequential steps by τ_1 and τ_2, respectively, the quenching process could be represented by the following scheme:

$$A + Cd \xrightarrow{\tau_1} B \xrightarrow{\tau_2} X \qquad (1)$$

By assuming that the SERS activity of B is lower than that of A by a factor α ($0<\alpha<1$), a simple calculation leads to the following formula for the SERS intensity $I(t)$ at time t, normalized by the initial intensity $I(0)$:

$$I(t)/I(0) = e^{-t/\tau_1} + \frac{\alpha\tau_2}{\tau_2-\tau_1}(e^{-t/\tau_2} - e^{-t/\tau_1}) \qquad (2)$$

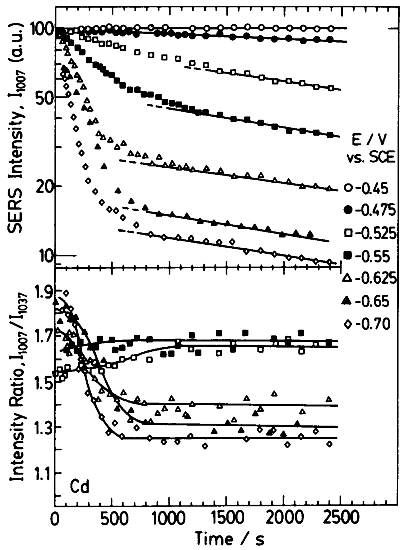

Fig. 2. Time courses of the pyridine SERS intensity (top) and its spectral shape (bottom) after potential steps from 0.0 V to a series of negative values.

Provided that the surface concentration of deposited Cd is sufficiently larger than that of the initial active site A, the first step is regarded as a pseudo-first-order process, with the time constant τ_1 inversely proportional to θ_{Cd}:

$$\tau_1 \propto \theta_{Cd}^{-1} \qquad (3)$$

As an example, a result of curve fitting according to Eq. 2 is given in Fig. 3(A) for the decay profile observed at −0.55 V. The experimental points lie fairly well on the simulated curve with τ_1=370 s and τ_2=4860 s. Similar treatments have been conducted on the decay profiles at a series of potentials. In some cases, the curve fittings were not very satisfactory in the very initial phase of the decay; this is probably related to the simultaneous occurrence of spectral change in the initial phase. However, since the extent of the I_{1007}/I_{1037} ratio variation is much smaller (at most *ca.* 35% for E=−0.70 V) than that of the I_{1007} variation itself, we could obtain τ_1 values within a reasonable error range. The τ_1 and τ_2 values thus estimated are summarized in Fig. 3(B) as a function of the reciprocal of θ_{Cd}. It is evident that τ_1 changes in fair agreement with Eq. 3, and that τ_2 is practically constant around 4000—5000 s, suggestive of an intramolecular decay process.

In Fig. 2 we note that the fraction of the SERS intensity lost during the first phase of quenching depends on the electrode potential. Qualitatively this is accounted for as follows. The SERS-active sites are most probably surface Ag^+ complexes having both pyridine molecule(s) and chloride ions as ligands.[6] We could reasonably assume that the composition of the ligand is a function of the electrode potential, since at least the chloride ions tend to desorb from the surface by negative polarization. Thus the identities of the SERS-active sites A and B, and hence the value of α, should all vary with the electrode potential, leading to the observed potential dependence of the quenching efficiency during the first phase.

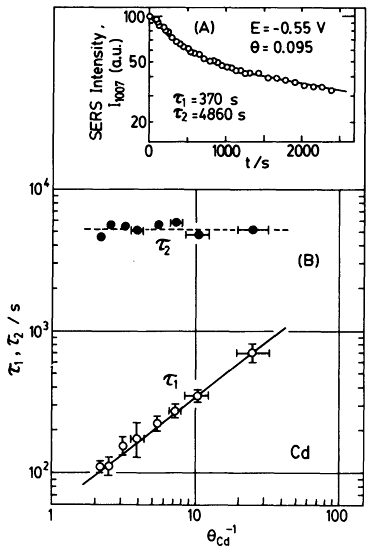

Fig. 3. (A) A typical result of analysis of the SERS intensity decay according to Eq. 2.
(B) Effect of θ_{Cd} on the values of τ_1 and τ_2.

If we now assume that the first phase of quenching (interaction between A and Cd) occurs *via* surface diffusion of the deposited Cd atoms, an order-of-magnitude estimate of its diffusion coefficient can be made as follows. The average distance L (cm) between a single active site A and a nearest-neighbor Cd atom at the completion of UPD is roughly the average distance between the Cd atoms, and is thus the reciprocal of the square root of its surface concentration, C_{Cd} (atoms cm^{-2}): $L \simeq C_{Cd}^{-1/2}$. As the Cd atom moves on the surface with a diffusion coefficient D (cm^2 s^{-1}) for a period t (s), the average departure l (cm) from the origin is approximated by $(Dt)^{1/2}$. We then regard the average lifetime τ_1 (s) of the initial active site A as the value of t such that $L \simeq l$; thus $\tau_1 \simeq (DC_{Cd})^{-1}$ or $D \simeq (C_{Cd}\,\tau_1)^{-1}$. Referring to Fig. 3(A) one obtains $D \simeq 2.5 \times 10^{-17}$ cm^2 s^{-1} from $\tau_1 \simeq 400$ s and $C_{Cd} \simeq 10^{14}$ atoms cm^{-2}. Since several constants related to actual surface geometry have been dropped in this calculation, it would be safe to give $D \simeq 10^{-16}$—10^{-18} cm^2 s^{-1} as a rough estimate. Although there is no data available for the surface diffusion coefficient of Cd on the Ag surface, the range of D deduced above covers remarkably well the homogeneous and heterogeneous surface diffusion coefficients determined recently by field ion microscopic techniques at 25 °C (D in cm^2 s^{-1}): 7.6×10^{-19} for W atom on W(110),[10] 6.8×10^{-18} for Re on W(211),[11] 2.9×10^{-15} for Ta on W(110),[12] 6×10^{-18} for Ir on W(110),[12] and 5.1×10^{-17} for Pt on Pt(110).[13] This could be indirect evidence for the occurrence of surface diffusion of Cd in the first phase of the SERS quenching.

If the first step in Eq. 1 is a simple association between A and Cd, stripping (oxidative removal) of the latter is expected to recover the original SERS intensity. To examine this point we followed the SERS intensity at a Cd-free potential, −0.2 V, before and after the Cd UPD at −0.625 V. By controlling the holding time at −0.625 V, we were able to make the stripping of the deposited Cd either within the first phase or after the quenching had reached deep into the second phase. The results are displayed in Fig. 4. As expected, when the potential was stepped back to −0.2 V after holding it at −0.625 V for 120—600 s, which is substantially within the first phase of the quenching (Fig. 2), the SERS intensity was almost totally recovered. On the contrary, stripping after a 2400-s holding at −0.625 V regenerated the

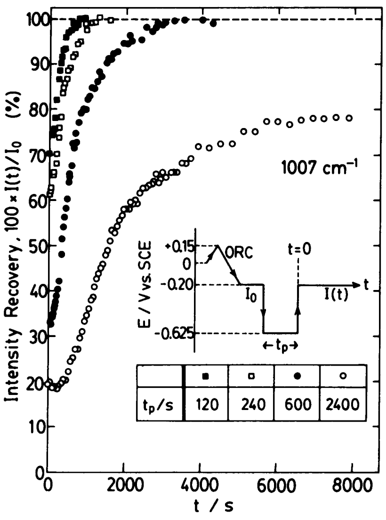

Fig. 4. Recovery of the pyridine SERS intensity observed by Cd stripping from the Ag electrode surface. The inset shows the potential programming.

original SERS intensity only to *ca.* 80%. The non-recovered fraction (20%) agrees fairly well with that calculated from Fig. 2 by means of Eqs. 1 and 2. These results indicate that the first step in Eq. 1 is of quasi-reversible nature, while the second step is an irreversible decomposition, though we are not yet sure about the actual mechanisms for these processes. Under an assumption that the initial SERS-active sites are sparingly soluble surface Ag^+ complexes having pyridine and Cl^- as ligands,[6] we tentatively propose that the second step of the quenching corresponds to an electron transfer from neutral Cd, being a reduced entity, to a surface Ag^+ center resulting in the disintegration of the Ag^+ complex. This may be in line with an observation by Kester,[4] that deposition of Tl onto the SERS-generating Ag/BTA interface leads to vanishing of BTA molecules from the surface, as evidenced by Auger spectroscopy.

The remarkable slowness of the intensity recovery noted in Fig. 4 suggests that the first phase of the quenching involves, in addition to a simple association between Cd and A, another kind of surface process. For instance, diffusion of state B toward the interior of the electrode bulk (or slight alloying), which could render the Cd atoms resistant to stripping, may be a candidate. This problem is however beyond the scope of the present paper.

The fact that Eq. 3 apparently holds fairly well at Cd surface coverages down to 0.04, or *ca.* 5×10^{13} atoms cm^{-2}, suggests, together with the assumption made in deriving Eq. 3, that the surface concentration of the initial active site A is on the order of 10^{12}—10^{13} sites cm^{-2}. Since a full coverage of pyridine on Ag corresponds to *ca.* 3×10^{14} molecules cm^{-2}, this again confirms the conclusion that the surface population of the SERS-active sites is considerably low.[1—3]

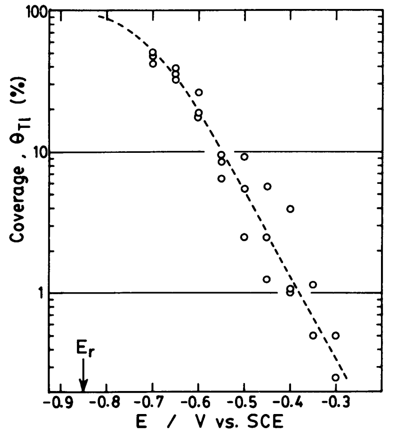

Fig. 5. Stationary Tl coverage on the electrode surface as a function of the electrode potential. $[Tl^+]=2.5\times10^{-5}$ M. E_r denotes the thermodynamic deposition potential.

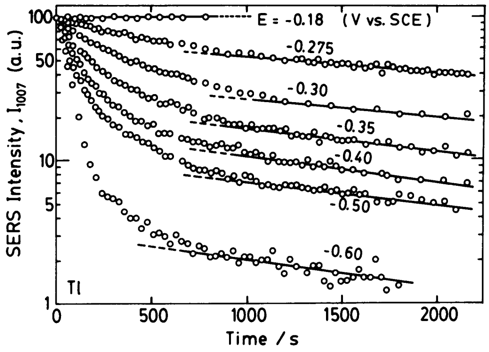

Fig. 6. Time courses of the pyridine SERS intensity after potential steps from 0.0 V to a series of negative values.

UPD of Tl. A series of similar kinetic measurements have been carried out also for the SERS-quenching effect of underpotentially deposited Tl. The potential dependence of the surface coverage, θ_{Tl} (E), determined by a procedure described above, is shown in Fig. 5. This result corresponds to a polarization time of 120 s, but we confirmed that the value of θ_{Tl} levels off within 50—100 s, as in the case of Cd UPD. Figure 5 reproduces a well-known tendency[9] that the surface coverage in the UPD region approaches unity as the potential approaches the thermodynamic deposition potential, E_r, which is −0.85 V *vs.* SCE in the present case.

Figure 6 is a counterpart of Fig. 2 (top). The pyridine SERS intensity decays again through a biphasic process, with the time constant of the first phase being dependent on the potential, while that of the second phase being nearly constant. This again

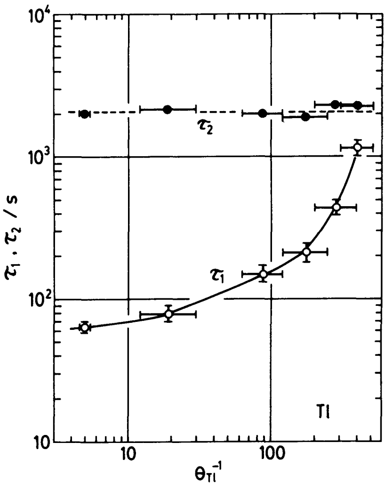

Fig. 7. Effect of θ_{Tl} on the values of τ_1 and τ_2.

suggests the occurrence of a sequential process as in Eq. 1. In comparison with the case of Cd UPD, the general quenching effect of Tl UPD is much more dramatic. For example, at $E=-0.4$ V, the stationary surface coverage of *ca.* 1% causes the SERS intensity loss of 93% in 2400 s (compare Figs. 5 and 6).

The biphasic decay profiles in UPD of Tl have also been successfully analyzed in terms of Eq. 2, and the τ_1 and τ_2 values thus derived are plotted in Fig. 7 against the reciprocal of θ_{Tl}. It is seen that the value of τ_2 is roughly constant at about 2000 s. The strong dependence of τ_1 on θ_{Tl} indicates that the first phase of quenching takes place *via* an interaction between the deposied Tl and the SERS-active sites. The nonlinearity between τ_1 and θ_{Tl}^{-1}, however, suggests that the interaction is of more complicated nature than a simple one-to-one encounter process of the two surface species.

Two major differences were noted between deposited Cd and Tl in quenching the pyridine SERS. First, whereas the UPD of Cd caused a change in the spectrum as well as the intensity in the first phase of the quenching, such a spectral change was not observed by the UPD of Tl within experimental error. This is in contrast with the case of the SERS in the Ag/BTA system,[4] where both intensity and peak frequency underwent a change by UPD of Tl. This would probably reflect a difference in the extent of vibronic state perturbation by the attack of Tl between the two systems. Second, the SERS intensity, once quenched by the UPD of Tl, was hardly recovered by stepping the potential to a sufficiently positive value, irrespective of the holding time at the quenching potential. In the case of UPD of Cd, as stated above, the intensity could be recovered if the quenching had been limited to the first phase. This result suggests that the Tl atom, in an encounter complex such as B in Eq. 1, is bound to the initial SERS-active site so strongly that it apparently undergoes no oxidation within the time range of the present measurements (on the order of 1 h).

So far, the SERS-quenching effect of underpotentially deposited Tl has been reported on the Ag/pyridine[1,3] and Ag/BTA[4] systems. In the former system, and also in the present work, a surface Tl coverage on the order of 1% causes a drastic quenching. In contrast, the SERS signal in the latter system is affected by UPD of Tl only at relatively high surface coverages, and becomes noticeable at potentials negative of -0.5 V *vs.* SCE.[4] Such a difference could qualitatively be accounted for within the framework of the present scheme (Eq. 1), by making a reasonable assumption that there is a difference between the two systems in the stability of the SERS-active site against the attack of Tl. A significantly low value of the solubility product for the Ag^+–BTA salt ($10^{-13.6}$),[14] in comparison with that for the Ag^+–pyridine salt ($10^{-9.8}$), suggests that the strength of the Ag^+–BTA bond is higher than that of the Ag^+–pyridine bond.

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