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Photon emission at metal/solution interface induced by electron injection from solvated electrons

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Light emission from metal, induced by electron injection from solvated electrons, was observed in an electrochemical system. The efficiency of emitted light increases drastically as electrode potential becomes positive. The high energy threshold of the spectrum increases as the electrode potential becomes positive by 1 eV/V. The peak energy also shifts positively as the electrode potential becomes positive, although the degree of the shift is much smaller. Various processes are considered as a possible mechanism for a photon emission. From the qualitative comparison of the results at platinum and gold electrode, the contribution of the inverse photoemission process to the bulk band states at the light emission process in the electrochemical system is suggested. The feasibility of applying this phenomenon to a novel spectroscopy is discussed.

I. INTRODUCTION

Although many important processes take place at solid/solution interfaces, e.g., electrochemical reaction, corrosion, and crystal growth, the understanding of these processes is still very immature. To fully understand how these processes proceed, one needs to know the electronic and morphological structures of solid surfaces and adsorbed molecules, i.e., reactants, intermediates, and products. Thus, the development of novel techniques to obtain the structural information of the solids and adsorbed molecules *in situ* is one of the most important subjects in the field of surface physical chemistry during the last decade. While *in situ* vibrational spectroscopic techniques provide the information of structures of adsorbed molecules¹ and morphological structures of solid surfaces can be determined by an *in situ* electrochemical scanning tunneling microscope with atomic resolution,² determination of surface electronic structure *in situ* is still very difficult in electrochemical systems. Although surface electronic states can be evaluated in ultrahigh vacuum by various techniques, e.g., ultraviolet photoemission spectroscopy (UPS)³ and inverse photoemission spectroscopy (IPS),⁴ they are not suitable for an *in situ* investigation of solids in solution.

McIntyre and Sass proposed a new technique which may be able to determine the electronic structure of electrode.⁵ They observed light emission from a metal when highly energetic chemical species exist in solution. They considered that light is emitted as a result of radiative relaxation of energetic electrons injected from an electron donor in solution, e.g., an organic anion radical, to empty electronic states in a metal, i.e., inverse photoemission (IP) process, and, therefore, the spectrum of emitted light reflects the electronic structure of the metal. Ouyang and Bard confirmed the observation and supported this mechanism. They concluded that the relaxation is mainly to Schockley-type surface state.⁶

The quantitative analysis of the observed spectrum is, however, not easy because of the complexity both in the

experimental procedure and in the interpretation. In the emission experiment proposed by McIntyre and Sass, the electrode potential is first pulsed to a very negative potential to generate the organic anion radical which acts as the electron injecting species, then it is pulsed to a positive potential so that the electron is injected from the anion radical to the metal.⁵ Usually this process is repeated many times to improve the *S/N* ratio. During the potential pulsing, decomposition of solvent, supporting electrolyte, added organic compound and/or impurities may take place. Decomposition of these species results in electrogenerated chemiluminescence (ECL) which interferes the emission from metal. The decomposed species sometimes polymerize and deposit on the electrode surface⁷ and, therefore, reproducibility of the experiment becomes low. Furthermore, a large potential modulation causes reconstruction and roughing of the surface which also lowers the reproducibility. Thus, a new experimental procedure should be developed.

The interpretation of the results is not satisfactory either. Although it has been considered that IP is the only cause of the photon emission in an electrochemical system, the origin and nature of the states which participate to the radiation process are not clear. One reason for the difficulties of the quantitative analysis is the complex scattering process of the energetic electrons in the metal. Light emission from the metal induced by electron injection with excess energies of a few eV has been observed also at metal-insulator-metal (MIM), tunneling junction (TJ),⁸ and scanning tunneling microscope (STM) systems.⁹ A totally different model is proposed for the light emission at these systems. In these cases, it is considered that the tunneling electron excites a certain surface plasmon mode that decays radiately.^{8,9} Thus, it seems to be necessary to evaluate the various contributions to the light emission process in electrochemical systems to analyze the emitted photon spectrum.

In this work, we have used chemically generated solvated electrons as electron injecting species so that the potential of the electrode is always kept at relatively posi-

tive potential region and decomposition of chemical species can be avoided during the emission measurement. We examined the origin of emitted light and discussed the feasibility of applying this method to determine electronic structure at the electrode/solution interface as a novel spectroscopy.

II. EXPERIMENTAL

Reagent grade hexamethylphosphoric triamide (HMPA: Wako Pure Chemicals Co. Ltd.) and sodium perchlorate (Aldrich Chemicals Co.) were used as solvent and supporting electrolyte, respectively. They were purified by usual manners¹⁰ and dehydrated in a vacuum. The electrolyte solution was prepared under a pure N₂ (99.999%) atmosphere. Solvated electrons were generated by dissolving sodium metal (Wako Pure Chemicals Co. Ltd.) in 0.2 M NaClO₄/HMPA solution. The prepared solution showed blue color with an absorption maximum at 770 nm which proves the formation of solvated electrons.¹¹ Solvated electrons generated in this manner lasted for more than several hours at room temperature.

Metal electrodes (Au and Pt) were prepared on clean glass by vacuum deposition using a pure metal wire (99.99%) as a source in 10⁻⁶ Torr vacuum. The temperature of the glass substrate during Au deposition was controlled by a hot-plate controller (Chino Co., DB-01-3) at 300 °C. The deposition rate and the thickness of the film were measured with a quartz crystal thickness monitor (ULVAC Co., CRTM-1000). Deposition rate (0.1 nm/s for Au and 0.01 nm/s for Pt) was controlled by changing the current passed through the tungsten wire around which metal wire was wound. Surface smoothness of the films was examined by scanning tunneling microscope (STM; Digital Instruments Co., NanoScope I).

Emission experiments were performed with a flow-type thin layer spectroelectrochemical cell made of Teflon.¹² The separation between the UV-quartz optical window and the working electrode was set to 100 μm with a Teflon spacer to minimize the absorption of emitted light by the electrolyte solution itself. The electrolyte solution was transferred from the supply flask to the thin layer compartment of the cell through a Teflon tube by positive N₂ pressure with constant flow rate so that solvated electrons around the metal electrode were not depleted. The potential of the working electrode was referred to the Ag/0.01 M AgNO₃ reference electrode. No electrochemical reactions due to residual moisture or other impurities were detected within the potential region examined in the present study (−3.4–0 V).

Light intensity was monitored with a photomultiplier tube (PMT: Hamamatsu Photonics Co. Ltd., R636) and a photon counter (NF Electronics, LI-574). Spectra of emitted light from metal electrode were obtained by using an imaging spectrograph (Jobin Yvon, CP-200) and a multi-channel detector (Hamamatsu Photonics Co. Ltd., IMD-C3330) with an image intensifier.¹³ Light emission measurements were carried out while the potential of the working electrode was either kept constant or swept be-

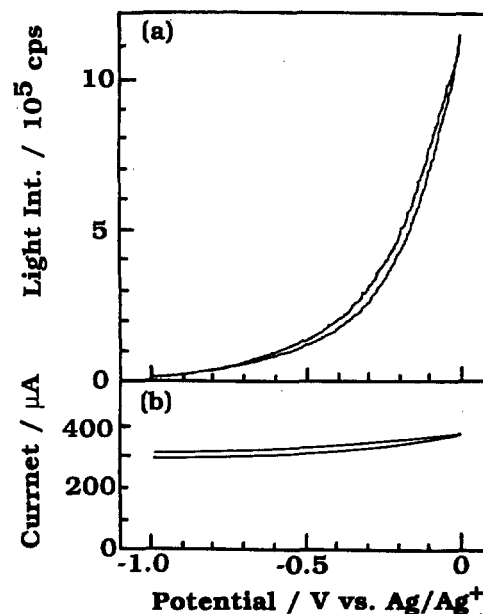


FIG. 1. Potential dependence of (a) emission intensity and (b) oxidation current at Au electrode in 0.2 M NaClO₄/HMPA containing solvated electrons. Scan rate: 20 mV/s.

tween −1.0 and 0 V. The positive potential limit (0 V) was chosen to avoid decomposition of the solvent.

All the measurements were carried out at room temperature.

III. RESULTS

The intensity of emitted light from Au and oxidation current were recorded simultaneously as a function of electrode potential and typical results are shown in Fig. 1. Although the oxidation current increases only slightly as potential U_w becomes positive, light intensity increases significantly. This means that the quantum efficiency of this process changes depending on electrode potential and is estimated as 10⁻⁸ at 0 V and 10⁻⁹ at −1.0 V.¹⁴ The intensity of emitted light and anodic current did not change with time as long as electrode potential was kept constant.

Typical spectra of emitted light from Au are shown in Fig. 2. It is clearly seen that both the high energy threshold E_{th} ¹⁵ and the peak energy E_p of the spectra increase as U_w becomes more positive. Figure 3 shows the potential dependence of E_{th} and E_p . E_{th} shifts linearly with U_w by 1 eV/V. The E_{th} is almost equal to the maximum energy of injected electron E_{inj} which is given by the energy difference between the Fermi level of the metal and the highest electronic energy level of solvated electrons in solution, i.e., $E_{th}/e = E_{inj}/e = -(U^0 - U_w)$, where U^0 is the redox potential of solvated electron.^{16,17} The potential dependence of E_p is smaller than that of E_{th} and the shift is ~0.2 eV/V. Thus, the shape of the spectrum is also affected by the electrode potential (Fig. 2).

Photon emission was also observed at Pt electrode, although the intensity was much weaker. A typical spectrum is shown in Fig. 2. The potential dependence of the spectra

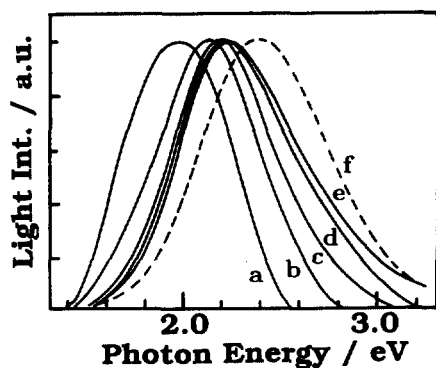


FIG. 2. Normalized spectra of emitted light from Au [(a)–(e);—] and Pt [(f); - - -] electrodes in 0.2 M NaClO₄/HMPA containing solvated electrons. The electrode potential was kept at (a) -0.8 V, (b) -0.6 V, (c) -0.4 V, (d) -0.2 V, (e) 0 V, and (f) 0 V. The emission peak intensities are normalized to that of the spectrum (e). The enlargement factors are (a) 15.3, (b) 4.4, (c) 1.5, (d) 1.2, and (f) 1.1, respectively.

at Pt has a tendency similar to that at Au as E_{th} shifts by 1 eV/V and E_p shifts to higher energy as electrode potential becomes positive. The E_p , however, is higher than that at Au by 0.1–0.2 eV at a given potential when U_w is more positive than -0.2 V as shown in Fig. 3. When the U_w is very negative, i.e., E_{inj} is very small, Spectra of Pt is very weak and it is very difficult to determine E_p and E_{th} . Therefore, only the values obtained at more positive potential than -0.7 V were shown in Fig. 3.

IV. DISCUSSION

There are various possibilities for the origin of the light emission at metal/electrolyte interfaces. The first possibility is the emission from chemical species in solution, e.g., ECL in which case the shape of spectrum is unique for a given system and should have no potential dependence.¹⁸ The linear relation between E_{th} and U_w mentioned above

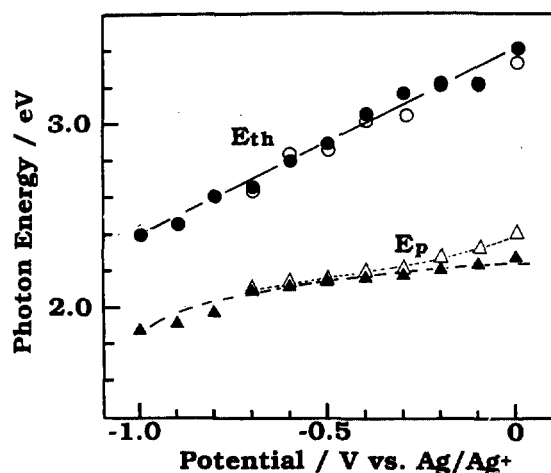


FIG. 3. Potential dependence of the high energy threshold E_{th} and the peak energy position E_p of the spectra at Au (●, ▲) and Pt (○, △) electrodes.

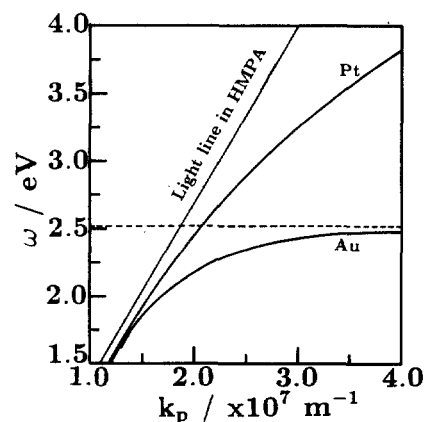


FIG. 4. Dispersion curves of surface plasmon at metal/HMPA interface.

excludes this possibility. Thus, it is certain that the light emission is from metal electrode induced by injected electrons.

The second possibility is a surface plasmon excitation decay process which is considered as the most important photon emission process in TJ and STM systems.^{8,9} At these tunneling junctions with a bias voltage of 2–5 V, injected electrons induce photon emission as they excite surface plasmon which decays radiatively. Surface plasmon is generally nonradiative but it becomes radiative when translational invariance along the surface is broken by roughness or irregularities at TJ⁸ or the presence of the microscope tip at STM.¹⁹ STM measurement showed that the surface of the electrode used here had relatively flat terrace of lateral dimension of a few tens–100 nm which is a reasonable size for photons to couple with the surface plasmon mode around 2–3 eV.²⁰ The total external quantum efficiency at TJ calculated by using the theory of Laks and Mills increases exponentially as bias voltage becomes larger.²¹ Similarly, the emission efficiency at STM system is enhanced as tip–sample voltage increases.⁹ In the present system, the quantum efficiency also increases drastically as U_w becomes positive, i.e., E_{inj} becomes larger. From the above considerations, the electromagnetic resonance at the metal surface seems to contribute for the photon emission process at the electrochemical system. Energy range of emitted photon can be estimated by the dispersion of surface plasmon at the metal/HMPA interface. The dispersion curves of Au and Pt in HMPA as well as light line in HMPA were calculated by using the tabulated dielectric constant ϵ_m and plotted in Fig. 4.²² Although the surface plasmon dispersion for Pt is drawn in Fig. 4, the resonance at Pt/HMPA interface is rather broad and strongly damped due to relatively large imaginary component of the dielectric constant of Pt.²³ The maximum of surface plasmon energy of Au is determined as ω for $k_p \rightarrow \infty$ and is indicated in Fig. 4 by dotted line. The surface plasmon excitation decay process can produce a spectrum of only photons with the energy lower than the maximum surface plasmon energy. The cut off energy at Au/HMPA interface is ~2.5 eV as shown in Fig. 4 and, therefore, the maximum energy of emitted photon is expected to 2.5 eV.

However, the energy of emitted photons from Au always extends right up to E_{inj} which can be much larger than 2.5 eV in some case. Furthermore, the photon emission was also observed at Pt electrode despite of the fact that the electromagnetic effect of surface plasmon does not operate due to the strong damping as mentioned before. Thus, the surface plasmon excitation decay process may be involved in the photon emission process but could not be the major contribution.

The other possible mechanism for the light emission process in this system is the charge transfer reaction inverse photoemission (CTIP) process proposed by McIntyre and Sass.⁵ In this process, some of energetic electrons, injected from radical species in solution, relax radiately to unoccupied bulk or surface states at lower energies of the metal. Importance of surface states in CTIP process was suggested by Ouyang and Bard⁶ and present authors.¹⁷ Electroreflectance (ER) spectroscopy study showed that the surface states of Au(111) are partly occupied at the potential of zero charge (pzc) in aqueous media (-0.16 V versus Ag/Ag^+ ²⁴) and become unoccupied only when the electrode is biased sufficiently positive.²⁵ The potential region examined in this study is relatively negative and it is reasonable to think that the surface states of Au are occupied and cannot contribute to the relaxation process. Furthermore, the surface state of Pt(111) is known to locate at higher energy than that of Au.²⁶ Thus, if the spectrum of emitted light reflects the distribution of surface states, photons emitted from Pt should have smaller energy than that of Au at a given potential. However E_p at Pt is almost the same as that at Au in the relatively negative potential region and shows more contribution of photons of higher energy in more positive potential region. These results suggest that the unoccupied electronic states of Pt to which injected electron relax are located at lower energy than that of Au contrary to the expectation. It seems, therefore, that the emitted photon spectrum reflects the relaxation of injected electrons to the bulk band states of metal rather than the surface states.

Large potential dependence of the emission intensity at the present system shown in Fig. 1 can be explained by considering the energy dependence of the radiative relaxation probabilities of electron in the spontaneous emission processes. It is known the probability becomes higher as the energy difference between the states is larger.²⁷ This means that the emission efficiency should be higher as E_{inj} becomes larger.

The above considerations suggest that the IP process to the bulk band states is the major contribution to the light emission from the metal in the present system. The spectrum reflects the density of the unoccupied states just above Fermi level and the relaxation probability of each transition. The spectrum of emitted light also contains the information of the electron transfer process, since the distribution of the injected electron energy was perturbed dur-

ing the electron transfer process at an interface. More quantitative analysis of the spectra is under way to investigate these contributions.

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