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Effect of the surface roughness on the spectral distribution of photoemission current at the silver/solution contact

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The use of an aqueous electrolyte containing dissolved CO_2 enabled revealing of an unusually intense photoemission from a bulk silver electrode. The observed cathodic photocurrent exhibits a sharp peak at ~360 nm corresponding to the energy of surface plasmons in silver. The amount and the spectral distribution of the photocurrent are strongly affected by the extent of roughness of the silver surface. In particular, an electrochemical roughening procedure, analogous to that leading to the surface enhancement of Raman scattering (SERS) at silver, causes appearance of a long tail on the low-energy side of the photoemission spectra. In consequence, significant photocurrents, corresponding to a quantum yield of ~7×10⁻³, are observed for the deliberately roughened silver electrodes illuminated with the wavelength of 514 nm, most frequently used in SERS experiments. It is postulated that this intense photoemission, discovered in the presence of CO_2 in the solution, equally takes place in the absence of scavengers. However, in the latter case no significant photocurrents can be detected as most of the photoemitted electrons (solvated or not) return back to the electrode. © 1995 American Institute of Physics.

I. INTRODUCTION

The role played by surface-plasmon polaritons (SPPs) is frequently evoked to explain the enhancement of such phenomena as hot-electron generation,¹ second-harmonics generation,² and Raman scattering.³ According to Endriz and Spicer,^{4,5} the pathway through which optically excited plasmons contribute to the photoemissive yield involves transfer of energy from decaying surface plasmons to a single electron. While most metals exhibit plasma frequencies corresponding to energies higher than 10 eV and thus exceed their work functions in vacuum, this is not the case of a low plasma frequency metal such as silver. In fact, the energies of bulk and surface plasmons for silver (3.8 and 3.6 eV), which lie in the range easily accessible to optical measurements, are, however, lower than the work function of the metal, equal to 4.3 eV. For this reason, vacuum photoemission experiments performed on Ag films involved surface modification (with caesium or polar organic molecules)⁶⁻⁸ in order to lower the effective work function. Adsorbed polar organic molecules have been found effective for the enhancement of photoemission of a cold Ag film as shown by the fact that a 0.66 L exposure to pyridine, methylamine, ethylamine, diethylamine, or 4-picolin lowered its work function from 4.3 to 2.5-2.8 eV.8 Pyridine and related dipole molecules affect the photoemission because of a nitrogen lone pair electronic orbital available for charge donation to the metal, and due to the chemisorption at right angles with respect to the surface, rendering the momentum effective. The absence of a clear correlation between the molecular properties such as dipole moment, polarizability, etc., and the threshold shift suggests that the acting dipole is created by charge transfer, as with Cs, which makes location of chemisorption sites important. Thus various surface treatments may be expected to cause

changes in the threshold and the magnitude of the photoemission current in a way similar to the case of surface enhancement of Raman scattering (SERS).

An alternative way to lower the work function of the electrons is to replace the metal/vacuum contact by a metal/ solution interface using an electrochemical cell configuration. An important advantage of such an arrangement is that, in addition to a decrease of the work function due to the higher optical density of the electrolyte (with respect to vacuum), a continuous modulation of the work function becomes possible simply by changing the electrode potential.

The effect of the surface-plasmon excitation upon photoemission of electrons at a nominally smooth surface of silver immersed in 1 N H₂SO₄ electrolyte, where protons were acting as electron scavengers, was studied by Sass et al.9 Due to a reduced threshold for electron injection into the electrolyte (ϕ =2.8 eV, lowered by almost 1.5 eV compared to the metal/vacuum interface), photoelectrons associated with the decay of surface plasmons could be directly detected under such conditions. The authors⁹ have observed a relatively intense peak of photoemissive yield close to 3.5 eV, corresponding to the surface-plasmon energy for Ag. Making the electrode potential more negative shifted slightly the position of the peak toward lower energies and strongly increased its intensity. Interestingly, a similar prominent peak was also observed for the photo-oxidative yield at an Ag electrode polarized anodically in neutral solution. It has been postulated⁹ that the excitation of surface plasmons results in a generation of excited electrons and holes very close to the Ag surface, where energy losses due to scattering are expected to be small compared to the energy of charge carriers excited in the bulk.

The measurements of photoemission into $1 N H_2SO_4$ electrolyte were also used by Neff *et al.*¹⁰ to study the optical excitation and decay of surface plasmons on high index faces of silver between Ag(100) and Ag(111). The authors have reported a strong crystallographic anisotropy of the photo-

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current component induced by surface plasmons which was observed for high index faces close to Ag(111) but disappeared for the faces close to Ag(100).

In this paper we report the results of photoemission studies at a polycrystalline silver/electrolyte interface, performed in the presence of CO_2 in the solution, using visible and near-UV light. Our recent reports^{11,12} revealed the existence of unusually large steady-state cathodic photocurrents on Ag immersed in the CO₂-saturated aqueous solutions, exhibiting a sharp maximum at \sim 360 nm, i.e., in the range of energies corresponding to surface plasmons on this metal. In the present work we particularly address the strong effect of roughness of the Ag surface upon the quantum yield and distribution of the photocurrent. The surface roughness has been shown to act as a momentum source facilitating SP excitation. Electrochemical roughening of the Ag electrode by oxidation-reduction cycles, as employed in our work, produces a randomly rough surface which consists of highly profiled metal structures, islands, colloidal aggregates, antennas, etc., exhibiting a spatial modulation of the electron density along the x-y plane, providing a whole spectrum of momentum transfer. Such an electrochemical roughening of the Ag surface constitutes a standard pretreatment allowing intense SERS effect of adsorbed molecules to be observed.

II. EXPERIMENTAL DETAILS

Photoelectrochemical experiments were carried out with two different light sources: a Spectra Physics model 2025-04 argon-ion laser (using either 334.0, 351.1, or 363.8 nm emission lines in the near-UV or the 514.5 nm visible line) and a 450 W xenon lamp (Osram) set in an Oriel model 6141 hausing. The photoemission yield was measured with an ISA II-20 monochromator with an 1:3.5 aperture and a spectral resolution of about 20 nm. The absolute intensity of the incident light from the monochromator was determined using a calibrated radiometer/photometer model 730 A from Optronic Lab. The photocurrent was measured at normal incidence of the intermittent light on the vertically mounted electrode with a Stanford Research Systems lock-in amplifier type SR530. Standard electrochemical equipment was used for potentiostating the working electrode and applying desired potential scans. All potentials were measured and quoted with respect to the HgO/Hg/0.1 M NaOH reference electrode, having a potential of 0.18 V versus a normal hydrogen electrode.

Silver electrode used for all experiments consisted of a rod (specpure 99.999% Ag from Johnson-Matthey) of a diameter of 0.7 cm embedded in a Teflon cylinder. The cross section of the rod (0.38 cm²) was exposed to the solution. Before each experiment, the Ag electrode was polished with fine emery papers and with a suspension of 0.3 μ m alumina powder until the surface was bright and highly reflecting. After being rinsed in twice distilled water, followed by sonification in an ultrasonic bath, the electrode was immersed inside the cell and kept in a deaerated 0.1 M NaClO₄ solution at open circuit for 10 min, before starting the measurements. To investigate influence of the surface roughness upon the photoemission yield, the freshly polished Ag electrode was

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roughened by a series of oxidation-reduction cycles performed in 0.1 M NaClO₄.

Solutions were prepared from twice distilled water and analytical grade NaClO₄. In order to remove residual heavy metal impurities, the solution was purified by galvanostatic pre-electrolysis conducted for 48 h between two platinum electrodes. Before each experiment oxygen was removed from the solution by a nitrogen flow. 99.99% pure carbon dioxide was passed through a column with activated carbon before being used to saturate the solution. The temperature of the solution was kept constant during all experiments by means of a Lauda thermostat type K4R. The two compartment, tight, Teflon electrochemical cell used in all types of measurements had a quartz window of optical quality. The light from the light source was focused on the Ag electrode by means of an optical lens on a spot of 7 mm diameter which covered exactly the whole surface of the working electrode. The platinum counterelectrode compartment was separated from the silver working electrode chamber by a Nafion membrane.



FIG. 1. Influence of the surface roughness on the quantum yield of photoemission at the silver/electrolyte interface; 0.1 M aq. NaClO₄ solution saturated with CO₂; Ag electrode potential -1.7 V.

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FIG. 2. Spectral distribution of the photoemission current (expressed as quantum yield per incident photon) as a function of the electrode potential for (a) the nominally smooth and (b) the roughened Ag; other conditions as in Fig. 1.

III. RESULTS

The most remarkable effect following upon electrochemical roughening of the Ag electrode was a strong increase of the photoemissive yield extending over near-UV and visible wavelengths (Fig. 1). Thus the quantum yield of photoemission (per incident photon), determined at -1.7 V in CO₂-saturated 0.1 M NaClO₄ solution, reached 24×10^{-3} for the roughened Ag electrode and 3×10^{-3} for the nominally smooth electrode, as compared to $\sim 1 \times 10^{-4}$ reported in Ref. 9 for H₃O⁺ ions acting as electron scavengers. The roughening of the Ag electrode consisted of several continuous oxidation-reduction cycles performed at 1 V/s in the potential range between -1.7 and +1.0 V, during 5 or 15 min. Such an activation resulted in a significant increase in the microscopic roughness of the surface. Apart from the general increase of the quantum yield, the electrochemical roughening of the Ag electrode produced a series of important changes in the photoemission spectrum. Thus with increasing surface roughness the photocurrent peak shifted from 360 to 380 nm, becoming, in addition, strongly asymmetric. All the spectra obtained for the roughened surface displayed a sharp cutoff on the high-energy side and broadened noticeably at longer wavelengths, exhibiting a long tail extending up to 650 nm. This is clearly seen in Fig. 1 with the enhancement factor of the photocurrent, due to the deliberate roughening, going from 8 at 360 nm to 30 at 514 nm.

Interestingly, a similar long tail extending to the red region has been observed¹³ in the extinction spectra of gas evaporated small Ag particles. Results obtained for samples with various degrees of particle aggregation strongly suggested, in agreement with theoretical calculations, that the surface-plasmon resonance in the low-energy region is to be associated with the increasing particle aggregation.

It is to be noted, in this connection, that following the 5 min roughening procedure, the dark cathodic current, which is mainly due to a reduction of CO₂, was at the most doubled compared to the current recorded for the nominally smooth surface. This indicates that the development of a microscopic roughness leading to very significant changes in optical properties of the Ag surface and to the strong enhancement of the surface-plasmon-induced electron emission affects only moderately the electrochemically active area of the electrode. Extending the roughening sequence from 5 to 15 min resulted in a further, more significant, rise of the dark current, indicative of the continuing increase of the electrochemically active surface area. In contrast, the photoemissive yield was practically insensitive to this extra increase of the surface area and even tended to decrease (cf. Fig. 1). Interpretation of this observation seems hazardous at this stage and will require a detailed description of the surface profiling. It is, however, pertinent to mention in this connection that, in a way similar to the photoemissive yield, the optimum SERS effect is usually attained after a relatively short sequence of the electrochemical roughening.

The effect of the surface morphology of Ag samples upon intensity of the SERS spectra of a model compound was recently investigated by Dawson *et al.*¹⁴ using scanning tunnelling and transmission electron microscopies. Interestingly, the enhancement of the SERS signals was improved with increasing the metal grain size. The observed behavior was explained in terms of greater internal damping of SPPs induced by their increased elastic scattering at the metal grain boundaries. The latter effect, favored by the small metal grain size (~40 nm in the work cited¹⁴), would result in a reduced Raman scattering.

The influence of the electrode potential upon the photoemission current on the nominally smooth and the roughened Ag surface is represented through three-dimensional plots and corresponding contour plots in Fig. 2. The spectra were recorded by scanning the electrode potential, at 100 mV/s, in the range of -0.4 to -2.3 V, at different wavelengths of incident light. The Ag electrode was roughened for 5 min in the same way as described above. Since excitation of surface plasmons may occur when the condition expressed by

$$\epsilon_{\text{metal}}(\omega_s) + \epsilon_{\text{medium}}(\omega_s) = 0$$

(where ϵ_{metal} , ϵ_{medium} are, respectively, the dielectric functions of the Ag and of the electrolyte and ω_s is the surfaceplasma frequency) is fulfilled, the excitation energy is expected to alter significantly with the potential of the electrode. Essentially, any electronic modification, localized in the close vicinity of the interface, will perturb both media. In the metal, in the immediate vicinity of the surface ($\leq \dot{A}$), electronic effects are predicted which can easily result in extremely strong electric fields of the order of 10^7 V/cm. It is considered that the dependence of the surface-plasmon excitation energy on the electrode potential originates mainly from the change in electron distribution in the metal surface, causing the change of the corresponding dielectric constant.¹⁵ On the other hand, application of a static electric field at the metal/electrolyte interface also significantly perturbs the ionic double layer. The contributions due to electronic effects in the metal and ionic effects in the electrolyte being correlated, the use of an ellipsometric detection enabled decoupling of the effects of the applied voltage on the electrons in the metal and on the ions in the electrolyte.¹⁶ In the present case regarding the SP enhanced photoemission on silver in the CO₂ containing 0.1 M NaClO₄ solution, the situation may be further complicated by a possible strong adsorption of CO₂ and/or its intermediate reduction products at the electrode surface.

The results shown in Fig. 2 fully confirm extremely large enhancement of the photoyield on rough surface of the Ag electrode. The characteristic peak of the photoyield, located at 360 nm for the nominally smooth and at 370–380 nm for the roughened electrode, becomes still more asymmetric and broadens significantly in the visible region at increasingly negative potentials. However, the position of the maximum of the surface-plasmon-induced photoemission peak remains unchanged going to negative bias potentials, in agreement with the literature data.¹⁵ At potentials more negative than



FIG. 3. Photoemission currents induced by the 514 nm laser line of varying power at the nominally smooth and the roughened Ag electrode in contact with 0.1 M aq. NaClO₄/CO₂ solution. E = -1.7 V.

-1.8 V, due to a competitive reaction of water reduction and to the strong gas evolution at the surface of the Ag electrode, the photoemissive yield weakened considerably, with the intensity of the peak at 370–380 nm decreasing much more rapidly than the tail in the green-red region of the light wavelengths.

Interestingly, the roughening procedure affected also the photocurrent threshold potential for the wavelengths corresponding to the surface plasmon resonance peak, i.e., at 360-380 nm. The result was a 150 mV positive shift of the threshold potential for the roughened electrode. This cannot be explained neither in terms of the classical theoretical model for the dependence of the photoemissive yield at a metal/electrolyte interface on the photon energy and the work function, i.e., so-called 5/2 law,¹⁷ nor by a change of the metal grain size.

As already pointed out, the electrochemical roughening of the Ag surface very strongly enhances optical excitation of surface plasmons and the related electron emission over a wide range of wavelengths. The extent of enhancement is considerably higher in the visible region than in the near-UV region where surface-plasmon resonance takes place. However, the intensity of the incident light normally used in our experiments was in the range of few milliWatts/cm², i.e., about three orders of magnitude lower than that usually employed in the SERS experiments. In Fig. 3 the photocurrents recorded for a nominally smooth and for a roughened Ag electrode in 0.1 M NaClO₄ solution saturated with CO₂ are represented as a function of the power of the incident 514 nm laser line. While the relation for the "smooth" electrode is almost linear over the whole range of applied light intensities, the slope of the corresponding curve for the roughened electrode tends to decrease with increasing light power. Thus the enhancement factor varies from 19 at 120 mW/cm² to 10 at 1500 mW/cm^2 . This observation is consistent with the fact that at higher light intensities an increasing number of photoelectrons are no more intercepted by the scavenging molecules. It is to be recalled in this connection that, in contrast with the situation prevailing at the metal/vacuum interface, in the case of the metal/solution interface only those among photoemitted electrons which react with the scavengers lead to a measurable photocurrent. However, while the scavengers serve to reveal the existence of the photoemission, the latter is obviously not suppressed in the absence of scavengers.

IV. CONCLUSION

The experimental evidence accumulated in this work points at the optically excited surface plasmons as being the origin of the unusually strong electron emission from silver in the CO_2 containing aqueous solutions. The presented measurements confirm in particular that electrochemical roughening of the Ag surface, similar to that usually employed before recording SERS spectra, leads to the strong enhancement of the photoemission current in the near-UV and, especially, in the visible range. Of particular importance with regard to the still discussed mechanism of the surface Raman enhancement is the observation that the standard roughening procedure extends in fact the spectral range of optical excitation of SPs on silver into the wavelengths most frequently used in SERS experiments (i.e., 514 nm). We postulate that the intense photoemission, revealed by the presence of CO_2 in the solution, equally takes place in the absence of scavengers. However, in the latter case no significant photocurrents can be detected as most of the photoemitted electrons (solvated or not) return back to the electrode. Future SERS experiments involving simultaneous photoemission current measurements (in the presence of suitable scavengers in the solution) are expected to clarify the relation existing between the above photocurrents and the intensity of the Raman signals.

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