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Combined roughness and electric polarization for the local-field enhancement of the second harmonic response from a silver-electrolyte interface

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A nanoscale rough silver film is electrodeposited from a silver cyanide aqueous solution and its growth is monitored by second harmonic generation (SHG). For growth by potential step into the diffusion controlled region, a maximum in the SHG intensity is always obtained for an equivalent silver film thickness of ~60 nm, based on the charge consumed. The SH intensity decreases for thicker but smoother films. A study as a function of an applied static electric field for an already grown film shows that the combination of nanoscale roughness and electric polarization is able to yield large enhancement of SH signal intensities. From a microscopic analysis of the data, it is shown that the nonlinear surface current perpendicular to the interface exhibits a nonlinear dependence with the applied potential, owing to the combination of roughness and electric polarization.

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I. INTRODUCTION

There has recently been a great interest in the optical properties of complex metallic nanostructures, in particular, nanoparticles of varied shapes, aggregated particles, nanoparticle arrays, and nano-rough surfaces.[1] This stems from the large local field enhancements available at these structures, arising from the surface plasmon resonance excitation and subsequently to the potential applications of these substrates for high sensitivity detection of compounds, e.g., in surface enhanced (resonant) Raman scattering [SE(R)RS]. The methodologies for the controlled production of aggregated particles starting from monodispersed colloidal solutions are now well established.[2] The different methods of production of these nano-rough metal film substrates include evaporation, chemical vapor deposition, and electrodeposition. All these routes aim at developing substrates with the largest local field enhancements but the exact details of relationship between the morphology and the field enhancements remain largely unavailable because of their random nature. Therefore, in parallel, there has been a considerable amount of theoretical and experimental work to investigate the linear and nonlinear optical properties of these systems, both in ensembles and at the single particle level.[3] Surfaces with random roughness are known to have peculiar spatial areas where field localization yields large magnitude local field enhancements. In order to map these areas, several attempts have been proposed with near-field optical imaging but recent work has demonstrated that far-field measurements could also probe the presence of these hot spots on the surface although with lack of spatial resolution.[4] In the nonlinear regime, the technique of second harmonic generation (SHG), the process whereby two photons at a fundamental frequency are converted into one photon at the harmonic frequency, has been shown to be a method of choice, to address both the problem of field enhancement at these surfaces and random roughness.

There are several reported studies of SHG on metal surfaces with nanoscale roughness.[1,5] Boyd *et al.*[1] demonstrated that the local field enhancement at a roughened silver-air interface can lead to large magnitude in the SH signals with enhancement factors on the order of $\sim 10^4$. These large factors are largely attributed to the concentration of the electric field at the tip of the structures, the so-called lightning rod effect, maintaining the dominant direction of the nonlinearity nearly perpendicular to the metal surface. These authors[1] provided a basis by which the surface local field enhancement at these nanoscale features could be quantified for several materials, including Ag. More recently, Stockman *et al.*[6] reported that the SH field becomes both strongly depolarized and dephased at these features.

In parallel, SHG at the metal-electrolyte interface has also been examined by several authors.[7–9] In their experiments conducted at the flat interface between a Ag(111) single crystal and an inert electrolyte, Guyot-Sionnest *et al.*[9] identified the nonlinear susceptibility component normal to the sample surface as the one component most sensitive to the applied static potential. In particular they obtained experimentally a linear dependence in the magnitude of the surface nonlinear current, perpendicular to the interface, with the applied static potential. This was also examined by Dzavakhidze *et al.*[7] and Schmickler *et al.*[10] who employed electronic density-functional calculations to determine theoretically the variation in the SH signal with the electrode charge in the presence and absence of specifically adsorbed ions.

In this work, we demonstrate that the combination of a random rough metal surface and an electric polarization of the interface yields large SH field enhancements with a dependence of the magnitude of the surface nonlinear current perpendicular to the interface reaching powers as high as four. Large SH intensities are thus collected for the largest applied fields and these results confirm that unusual SERS spectra can be collected from nanorough substrates polarized with an external static field.[11]

II. EXPERIMENTAL SECTION

The silver deposition on glassy carbon (GC) was performed following the work of Márquez *et al.*[12] The electrochemical experiments were performed using a three-electrode cell with the electric potential at the GC-solution interface controlled by an EG & G 361 potentiostat. A silver wire inserted directly into the solution served as the reference electrode. For direct comparison with previous work, all values of potential in the solutions used here were subsequently referenced with respect to the saturated calomel electrode which has a potential of 0.242 V vs the standard hydrogen electrode. The nonlinear optical studies were performed using a femtosecond laser delivering at 800 nm pulses with a duration of about 70 fs with a repetition rate of 80 MHz. The average power at the laser exit was about 1 W. The incoming fundamental beam polarization was defined with a half-wave plate and a low-pass filter was used to remove any SH light prior to the cell. The incoming fundamental beam was impinging at the rough silver-electrolyte interface at about 45° from the aqueous phase and the outgoing harmonic beam was separated from the fundamental beam reflected from the interface with a high-pass filter. The harmonic beam polarization was set with a half-wave plate and then passed through a spectrometer before detection with a charge coupled device camera. The SHG band at 400 nm was adjusted with a Gaussian function, thereby removing the background consisting of noise and multiphoton excited luminescence photons.

III. RESULTS AND DISCUSSION

The cyclic voltammogram for the silver deposition from the 5 mM AgCN/0.2 M KCN/0.5 M KOH solution is shown in Fig. 1. This gives the classic diffusion controlled peak at −1.24 V for the reduction of the $[\mathrm{Ag(CN)_2}]^-$ complex to yield metallic silver, and a nucleation loop at −1.09 V on the reverse scan, consistent with the formation of a new metallic phase on the GC electrode. The onset for the anodic process occurs at −0.81 V yielding a classical surface-controlled symmetrical stripping peak.[12,13] It is known from literature that deposition from this solution yields hemispheroidal particles with the number density of the nuclei increasing exponentially with the overpotential, up to the peak potential.[12] The application of a potential step into the diffusion controlled region of the electrodeposition process yields the expected falling current-time I-t transient (the I vs $t^{-1/2}$ plot is linear) for the film growth.

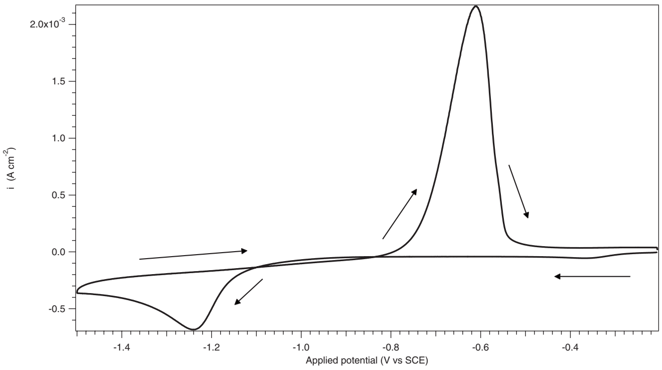

FIG. 1. Cyclic voltammogram recorded at the GC electrode in a 5.0×10^{-3} M solution of AgCN in 0.2 M KCN /0.5 M KOH solution. The potential scan rate was 50 mV s^{-1}.

SHG from polarized metal-electrolyte interfaces has been described in the past through a nonlinear current model. Here, three phenomenological parameters, also called the Rudnick and Stern parameters $a(\omega)$, $b(\omega)$ and $d(\omega)$,[14] are introduced for the three nonlinear currents viz. the surface currents perpendicular and parallel to the interface and the bulk current perpendicular to the interface arising from the skin layer effect.[14] In the latter model, the p-polarized SH intensity, hereafter referred to as the P_{OUT} intensity, can be written as[7]

$$\frac{I_{2\omega}}{I_\omega^2}=\frac{8\pi e^2}{m^2\omega^2c^3}\left|\frac{\varepsilon_s(\omega)\varepsilon_s(2\omega)\varepsilon(\omega)[\varepsilon(\omega)-\varepsilon_s(\omega)]}{\varepsilon(2\omega)+s(2\omega)}\right.\\ \left.\times(P\cos^2\psi+S\sin^2\psi)\tan\theta\right|^2, \tag{1}$$

where

$$P=\frac{a(\omega)\dfrac{\varepsilon(2\omega)\varepsilon_s(\omega)}{\varepsilon(\omega)}\sin^2\theta-b(\omega)\dfrac{2s(\omega)s(2\omega)}{\varepsilon(\omega)\varepsilon_s(\omega)}\cos^2\theta+\dfrac{1}{2}d(\omega)}{[\varepsilon(\omega)+s(\omega)]^2}, \tag{2}$$

$$S=\frac{d(\omega)}{2\varepsilon(\omega)[\varepsilon(\omega)+s(\omega)]^2}, \tag{3}$$

and

$$s(\omega)=\frac{[\varepsilon(\omega)-\varepsilon_s(\omega)\sin^2\theta]^{1/2}}{\cos\theta}\varepsilon_s^{1/2}(\omega). \tag{4}$$

Here, e, m, and c are fundamental constants, i.e., e is the electronic charge, m is the electron mass, and c is the speed of light. ω and 2ω are the fundamental and harmonic frequencies respectively. $\varepsilon(\omega)$ and $\varepsilon_s(\omega)$ are the bulk optical dielectric constants of the metal and the electrolyte solution, respectively, θ is the angle of incidence, and ψ is the angle of the polarization vector with respect to the plane of incidence, with $\psi=0°$ corresponding to the fundamental p polarization, hereafter referred as p_{IN}. The SH response from the metal-electrolyte interface is described principally through the surface current perpendicular to the interface, i.e., the $a(\omega)$ co-

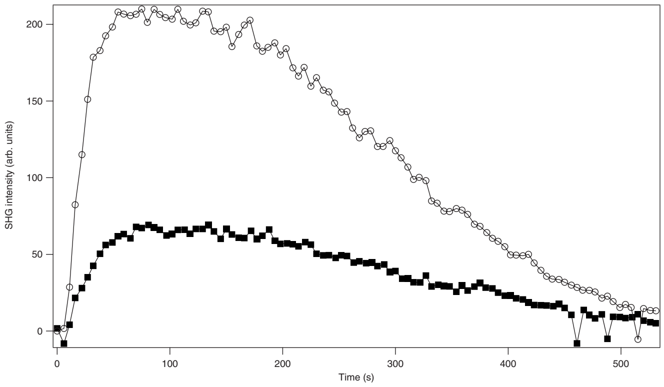

FIG. 2. The SHG intensity recorded in the p_{IN}-P_{OUT} polarization configuration at a GC electrode during the growth of a Ag film by a potential step to −1.35 V (■) and −1.55 V (○), in a 5.0 $\times 10^{-3}$ M solution of AgCN in 0.2 M KCN/0.5 M KOH solution.

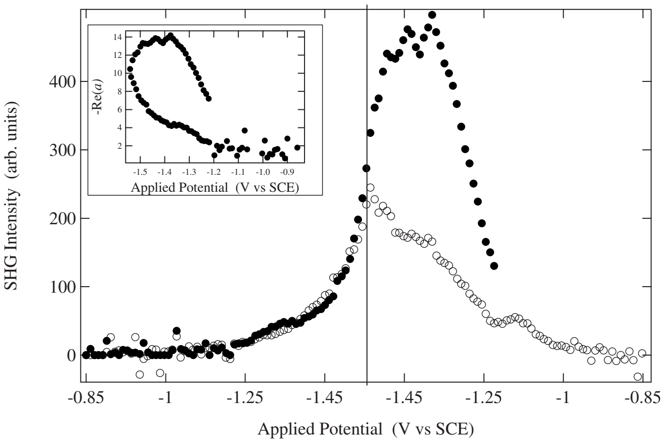

FIG. 3. SHG intensity recorded in the p_{IN}-P_{OUT} (●) and p_{IN}-S_{OUT} (○) polarization configurations in a 0.2 M KCN/0.5 M KOH solution for an electrodeposited Ag film (37 nm) as a function of the applied potential. The potential was scanned from −0.85 to −1.55 V (the vertical line marks the potential −1.55 V). Inset: The variation of—Re $a(\omega)$ with the potential (see text).

efficient, the dependence of which on the applied static field yields in turn the SH intensity's dependence. For a perfectly smooth interface $b=-1$ and $d=1$, irrespective of the frequency, and $a(\omega)$ is negative and of the order of unity.

Monitoring the SHG signal in the p_{IN}-P_{OUT} configuration during the deposition process yields the data shown in Fig. 2. For the potential step to −1.55 V, into the diffusion controlled region, an initial sharp increase in the SH intensity is observed before saturation and decrease. This rapid initial increase is due to the growth of the silver particles on the GC electrode,[12] starting from nuclei densities in the range 10^7 cm^{-2}. The dependence of the SH intensity in this regime depends not only on the amount of silver deposited but also on the morphology of the film and the possible excitation of surface plasmons in the particles. Surface plasmons can be excited in such a nanorough film owing to the loss of the translation invariance along the plane of the interface. Beyond an equivalent film thickness of about 60 nm, as determined from the charge consumed during the process, the SH intensity then levels off and a monotonous decrease in the SH intensity with increasing film thickness is then found. This film thickness at the maximum of the SH intensity is obtained irrespective of the value of applied potential step as long as this value is in the diffusion controlled growth region. At this SH peak intensity, the roughness must then be maximum. If we consider the growth to be that of hemispheroids, the film morphology then corresponds to that of touching hemispheroids. Hence, a simple geometrical model yields a maximum height of $3d$ where d is the film thickness of the corresponding equivalent flat film. The height of the hemispheroids is therefore ~ 180 nm. Such a morphology is similar to that found by Márquez *et al.*[12] in their study of silver deposition on GC and Si(111) from alkali cyanide solutions. Beyond the thickness of 60 nm, the film loses its roughness and so its surface enhancement. The SH intensity eventually falls back to that of a flat continuous silver film. The latter intensity is about 10 times smaller than that observed at the peak and is the same irrespective of the applied potential; see Fig. 2.

In order to examine this enhancement in greater detail, the growth of the silver deposit to an equivalent thickness of only ~37 nm was carried out using the potential step method as above. This was to ensure that the SH intensity enhancement regime is dominated by the surface roughness principally. The film, once grown, was then removed from the growth solution and placed in the KOH/KCN electrolyte, without Ag^+ ions, and the SHG intensity from this surface was then investigated as a function of the applied potential over the range −0.85 to −1.55 V. Figure 3 shows the variation in the SH intensity as a function of the potential measured in the p_{IN}-P_{OUT} and p_{IN}-S_{OUT} polarization configurations. In the latter configuration, the nonvanishing SHG intensity collected confirms that the film is rough at the nanoscale since no signal is expected for a perfectly smooth metal-electrolyte interface. This configuration also yields a SHG intensity sensitive to the applied static field. In the p_{IN}-P_{OUT} polarization configuration, where the response is dominated by the $a(\omega)$ parameter, the sharp rise in the SH intensity at the extreme voltages underlines that the nonlinear surface current perpendicular to the interface is greatly affected by the film roughness and the electric polarization. As seen from the inset of Fig. 3, obtained by inverting Eq. (1) using a real valued $a(\omega)$ parameter with a normalization to the polarized flat film and a fundamental wavelength of 800 nm, the applied static field dependence of the $a(\omega)$ parameter strongly deviates from a linear dependence observed for the smooth silver film[9] in the range +0.7 to −10. A value of $b=-1$ was also used. A hysteresis is also observed with the applied potential and this is attributed to the nonnegligible role of the adsorbing CN^- ions of the electrolyte solution. In particular, it is expected that with cyanide desorption (dependent on the relative stability of AgCN, $\mathrm{Ag(CN)}_2$, and $\mathrm{Ag(CN)}_3$ surface complexes) at these negative potentials,[13,15] the electronic tail gets more polarizable. It is therefore concluded that the combination of surface roughness and electrical polarization yields overall SHG intensities much larger than when only one enhancement factor, viz., roughness or field, is present. The direction normal to the electrode interface is still dominant, as evidenced from the higher dependence of the SH intensity with the applied potential in the p_{IN}-P_{OUT} polarization configuration in contrast to that observed for the p_{IN}-S_{OUT}. The nonvanishing intensity recorded in this latter polarization configuration also calls for an extension of the SHG intensity dependence with the surface currents. In particular, the nanoscale roughness will yield a dependence of the p_{IN}-S_{OUT} intensity with the two parameters $a(\omega)$ and $b(\omega)$.

IV. CONCLUSION

In summary, it has been demonstrated that local field enhancements as monitored by SHG can be greatly increased by the combined action of the electric polarization and the nanoscale surface roughness. In these conditions, the nonlinear surface current perpendicular to the interface exhibits a nonlinear dependence with the applied potential. These experiments were conducted in a far-field configuration where the SH signal is averaged over the whole beam area. It is highly likely that probing at the nanoscale would yield even larger enhancements.

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