

ARTICLE

Plasmonic Field Enhancement for Vibration Spectroscopy at Metal/Water Interfaces[†]

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Electrochemical (EC) reactions play vital roles in many disciplines, and its molecular-level understanding is highly desired, in particular under reactions. The vibration spectroscopy is a powerful *in situ* technique for chemical analysis, yet its application to EC reactions is hindered by the strong attenuation of infrared (IR) light in both electrodes and electrolytes. Here we demonstrate that by incorporating appropriate sub-wavelength plasmonic structures at the metal electrode, the IR field at the EC interface can be greatly enhanced via the excitation of surface plasmon. This scheme facilitates *in situ* vibrational spectroscopic studies, especially using the surface-specific sum-frequency generation technique.

Key words: Metal water interfaces, Surface plasmon excitation, Extraordinary optical transmission

I. INTRODUCTION

Electrochemistry is among the most important disciplines in modern science and industry, playing key roles in numerous processes including electrosynthesis, electrolysis, and many others [1]. However, our understanding on electrochemical (EC) reactions regards mostly energetics, which is based on conventional *I-V* analytical tools [2]. The *in situ* identification of unknown species as intermediates, products, and characterization of real-time molecular bonding-geometry, orientation, and conformation, remains a scientific challenge [3]. Such molecular-level information must be obtained with species-focused analytical tools, for example, the vibration spectroscopy [4, 5]. The sum-frequency vibrational spectroscopy (SFVS) can be regarded as a surface-specific version of vibration spectroscopy, which has enabled molecular-level studies of various interfacial systems, in particular liquid interfaces, over the past two decades [6]. Still, its application on this topic was limited, because most EC interfaces are not accessible in the IR range of interest, as both electrodes and electrolytes are often strong infrared (IR) absorbers. To overcome this, we exploited the surface plasmon (SP) resonance at the gold electrode, and achieved *in situ* vibration spectra of a thiol self-assembled monolayer under redox processes, providing real-time information of the reactions [7].

Nonetheless, the field enhancement by SP resonance decays rapidly when the absorption of the electrolyte grows. In particular, water is one of the most important and widely used electrolytes [8], yet it also has very intense and broad infrared absorption bands in OH vibration regimes. It turns out that the field enhancement by conventional SP excitation schemes on smooth metal films (such as the Kretschmann configuration used in our previous study [7]) is not strong enough for probing vibration spectra of water itself. In this study, we propose the integration of sub-wavelength nano-gratings on metal electrodes to boost up the field enhancement. In analogue to the effect of extraordinary optical transmission (EOT) effect [9], the guided field through metallic trenches couples to the SP and compensates for its loss. With optimal parameters, the IR field can be enhanced appreciably even on water absorption peaks. Such plasmonic structures are readily employed to SFVS, and are also generally applicable to other IR spectroscopy techniques of EC interfaces.

II. METHOD

To analyze the electric field at designated interfaces, we performed numerical simulations with the radio frequency module using the finite element method with Comsol Multiphysics 3.5 [10]. Floquet periodicity boundary condition is used for oblique incidence [11].

III. RESULTS AND DISCUSSION

A. Field enhancement by the Kretschmann configuration

The SP excitation on smooth surfaces is usually via Otto [12] and Kretschmann [13] configurations. The

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schematics of the latter is illustrated in Fig.1(a). The SP at the metal and underneath dielectric interface can be excited when its energy and momentum both match with that of the incident light. The resonant angle of the incident light is found to be [14]:

$$\sin\theta_0 = \sqrt{\frac{\varepsilon_{\text{metal}}\varepsilon_{\text{dielectics}}}{(\varepsilon_{\text{metal}} + \varepsilon_{\text{dielectics}})\varepsilon_{\text{prism}}} \quad (1)$$

Given the prism material, metal, and dielectric being silicon, gold, and water, respectively (related dielectric constants can be found in Refs.[15, 16]), the resonant angle is found to be 24.3° at 3300 cm^{-1} , near the IR absorption peak of water. The spatial distributions of electric field near a 20 nm-thick gold film on (right panel) and off (left panel) resonance are shown in Fig.1(b). It is seen that at the gold/water interface, the electric field is enhanced upon the SP resonance but only for about 2 times due to the strong absorption of water. In contrast, the SP enhancement of the IR field at $\sim 2900\text{ cm}^{-1}$ can be more than an order. Since the field strength in the latter case was essential for a reasonable signal-noise-ratio (SNR) in SFVS experiments, the above scheme is not enough for probing water spectra in this frequency range (around 3300 cm^{-1}).

B. Field enhancement with sub-wavelength nano-grating

To boost up the field enhancement, we utilize plasmonic-structured gold films instead of smooth ones. The schematic of the structure is shown in Fig.2(a). Here, instead of prism, we consider a planar silicon wafer that supports the gold film. In this case, the momentum mismatch between the SP wave and free-space IR wave is compensated by the periodic grating structure engraved on gold [14]. When SP is excited, there is the relation that:

$$\sin\theta_0 = \frac{m\lambda_{\text{IR}}}{p_g} \pm \sin\theta_2 \quad (2)$$

Here θ_0 is the same angle as in Eq.(1), m is a positive interger, λ_{IR} is the wavelength of the IR light in silicon, p_g is the periodicity of the grating, and θ_2 is the refractive angle of the IR beam in the silicon wafer (Fig.2(a)). For experimental purpose, the IR incident angle is preferentially the Brewster angle to minimize the θ_1 being the Brewster angle from the air to silicon, and θ_2 is thus determined. The periodicity (p_g) for exciting the m th-order SP wave can then be obtained.

Still, for a given m , there are two possible p_g values corresponding the + and - signs in Eq.(2). With the + (-) sign, the SP wave propagates along the same (opposite) direction with the parallel component of the incident IR wave, as shown in Fig.2(a) (Fig.2(b)). With $m=1$, and at 3300 cm^{-1} , we found $p_g(+)=6.45\text{ }\mu\text{m}$ and $p_g(-)=1.27\text{ }\mu\text{m}$, respectively. The field distributions for the two different periodicities are plotted in Fig.2

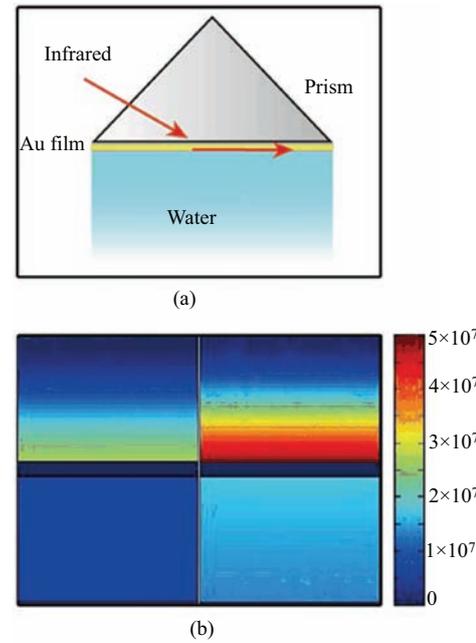


FIG. 1 (a) The Kretschmann-Raether configuration for SP excitation using a coupling prism. (b) Spatial distributions of electric field with resonance on (incident angle= 24.3° , right panel) and off (incident angle= 16.2° , left panel) at 3300 cm^{-1} , the thickness of the gold film is 20 nm.

(c) and (d), for a 20 nm-thick gold film and 50 nm slit width. Clearly $p_g(-)$ leads to a much greater electric field strength at the gold/water interface (note the different scales) compared to not only the grating structure with $p_g(+)$, but the smooth film as well.

To understand this effect, we first note that the reduced field enhancement at 3300 cm^{-1} is due to the strong absorption of water. Hence a simple picture for the additional enhancement by the grating structure is that through each slit, the guided field can couple to the SP wave and compensate for its loss. The coupling is possible as the guided field at the slit has an evanescent component, as in the case for EOT [17]. Compared to $p_g(+)$, $p_g(-)$ yields a larger number of slits per unit length, therefore a better compensation for the loss. According to Eq.(2), $p_g(-)$ has the smallest possible value at $m=1$, which thus is the optimal period for our structure.

There are two more desirable features of the field distribution in Fig.2(d) for SFVS studies of EC interfaces. First, the strongest field does not locate inside the slit, but at the nearby metal/water interface that we aim at. This is in contrast with plasmonic-structures designed for enhanced far-field transmission [18], which has the field concentrated inside the slit. Second, with the SP wave propagating oppositely to the incident IR wave, it is easier to achieve a large angular separation between the sum-frequency beam and upconverting visible (or NIR) beam reflected from the electrode [19], which fa-

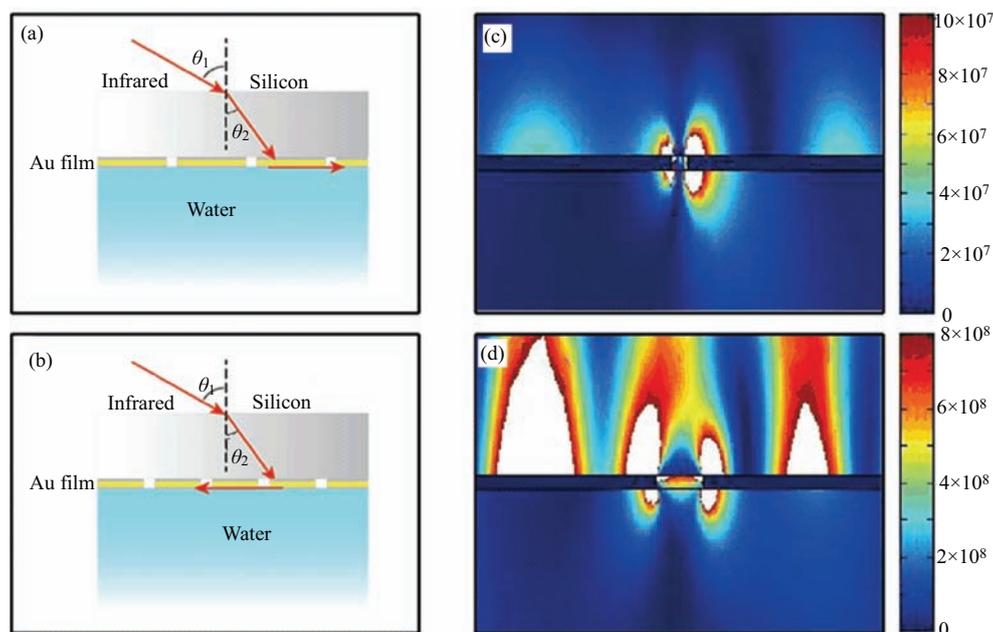


FIG. 2 (a) and (b) Schematics of the SP excitation at the interface between water and gold nano-grating deposited on a flat silicon wafer. (c) and (d) Spatial distributions of electric field for (a) and (b). The white parts in (c) and (d) represent the most intense part of the field.

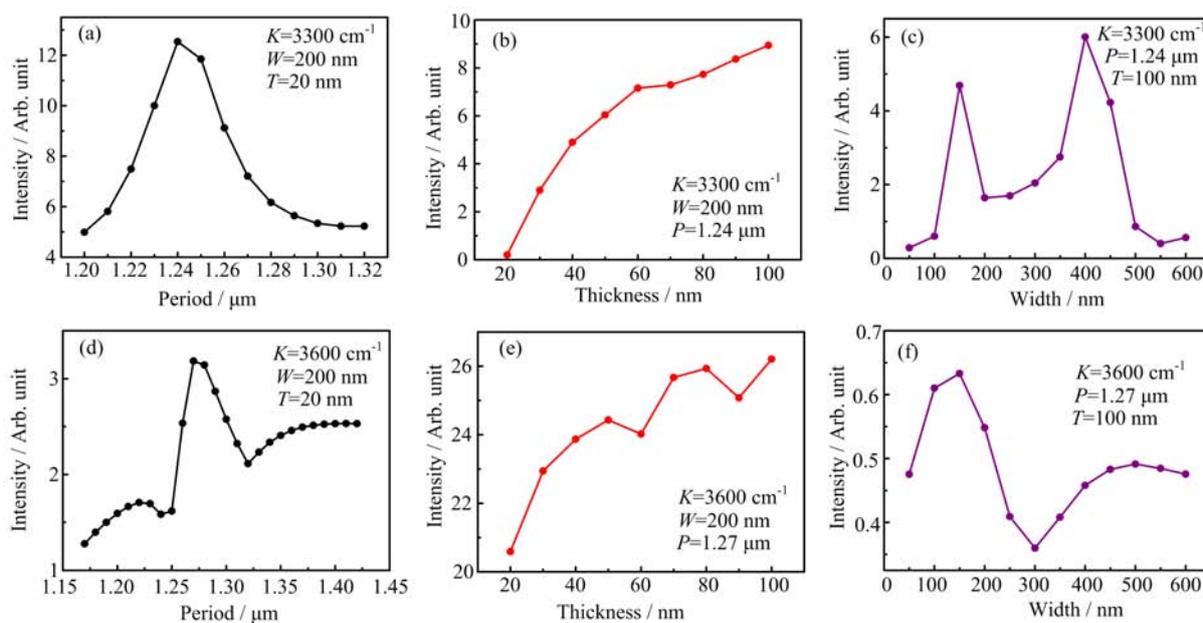


FIG. 3 (a)–(c) Integrated interfacial field intensity along the gold/water interface with different parameters at 3300 cm^{-1} , (d)–(f) 3600 cm^{-1} . K , W and T refer to the IR frequency, slit width, and gold film thickness, respectively.

cilitates the detection and increases the SNR.

C. Optimal parameters for the nano-grating

Besides the periodicity, the interfacial field strength is also dependent on the slit width and film thickness. We calculated the integrated field intensity along the

gold/water boundary with different parameters to obtain the optimal structure. Figure 3 (a)–(c) ((d)–(f)) show the field intensity at various periodicity, film thickness, and slit width, respectively, for 3300 cm^{-1} (3600 cm^{-1}). In contrast to the smooth film, the intensity actually increases with the film thickness between 20 and 100 nm (Fig.3 (b) and (e)). This is another

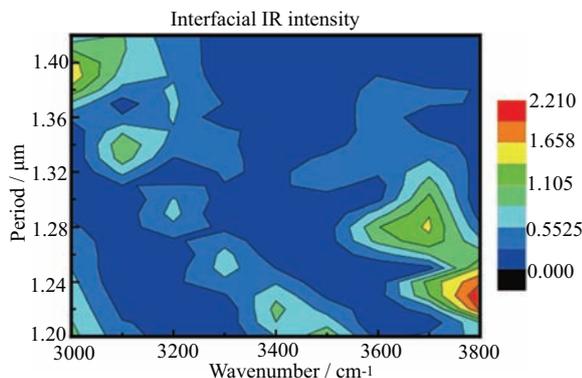


FIG. 4 The integrated IR field intensity at the gold/water interface (normalized to the period) versus the IR frequency. The gold film thickness is 100 nm, and the slit width is 150 nm.

desirable feature of the structure, as thicker films are more robust under both the laser irradiation and electrical cycling. Overall, at both frequencies, a slit width of around 150 nm, and a film thickness of 50–100 nm are appropriate.

However, due to the limited bandwidth of the SP resonance, a single periodicity cannot cover the entire water absorption band. This is better illustrated in Fig.4, showing the evolution of resonant frequencies with the periodicity. Therefore, it is preferential to combine two different periods, for example, 1.24 and 1.27 μm to achieve an enhancement for the entire OH stretch vibration band.

IV. CONCLUSION

We utilized a sub-wavelength nano-grating structure to boost up the IR field at the gold/water interface for SFVS studies on EC reactions. With appropriate structural parameters, our simulations show such a scheme can greatly enhance the interfacial IR field compared to the smooth film, enabling the detection of interfacial water spectra using SFVS. At 3300 and 3600 cm^{-1} , the optimal grating periods are 1.24 and 1.27 μm , respectively, and the optimal film thickness and slit width are at 50–100 and 150 nm.

V. ACKNOWLEDGMENTS

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