Near-Field Heating, Annealing, and Signal Loss in Tip-Enhanced Raman Spectroscopy

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We studied the morphological changes of “hot” spots in gap-mode tip-enhanced Raman spectroscopy (TERS) experiments by monitoring both the Raman spectra and topographic images of amorphous Au surfaces that were covered with a benzenethiol monolayer. Significant roughness reduction of the Au surfaces in the vicinity of the location of the TERS measurement together with irreversible signal loss was observed. To understand this phenomenon, a numerical simulation was performed and the result implies that it was the Joule heating generated by the highly enhanced electromagnetic field in the “hot” tip−sample nanogap that locally annealed the Au surface. Considering that the mobility of the atoms on top of an Au surface is high and the reduction of the local roughness is significant, we propose that the TERS signal loss is mainly caused by two mechanisms: reduction of electromagnetic enhancement caused by the degradation of the “hot” site and concomitant surface diffusion of the adsorbates.

Introduction

Signal instabilities in the forms of signal losses and spectral fluctuations with time[1−4] have been widely observed in surface-enhanced Raman spectroscopy (SERS) and tip-enhanced Raman spectroscopy (TERS). Studying these phenomena is not only interesting for understanding the mechanisms of SERS but also important for developing SERS/TERS into a reliable analytical method, which can afford rich chemical information with a single-molecule sensitivity. The signal instability has been observed on different SERS substrates in various experimental conditions, e.g., rough metal electrodes in an electrochemical environment,[5] metal films by cold deposition in ultrahigh vacuum,[6,7] nanogaps between metal structures at ambient temperatures,[8,9] etc. In this work, we focus on the “hot” nanogaps, because they are supposed to give the largest enhancement, allowing single-molecule spectroscopy, and have great potential in the area of the SERS-based chemical sensor. So far, most of the studies of the spectral instabilities in single-molecule SERS experiments focused on the dynamics of the analytes at “hot” sites, such as diffusion and rotation of the adsorbates,[10,11] the variation of the charge transfer between the molecule and the surface induced by dynamics of the adsorbates,[4] reaction with oxygen,[12] etc. However, to the best of our knowledge, no direct observation of the degradation of “hot” gaps themselves has been reported so far. In the following, “hot” refers to “high enhancement”.

It is well-known that ultrafine metal structures are instable. For instance, the melting point of metal nanoparticles can be much lower than that of the corresponding bulk materials;[13] nanostructures can be reshaped or fragmented under the irradiation of pulse lasers or strong continuous wave lasers.[14] Surprisingly, morphological changes of SERS substrates, which are covered by nanostructures, have not been reported so far. One of the main reasons is that the power of the excitation laser used in SERS or TERS experiments is normally ∼1 mW or lower, much lower than the power thought to be needed to cause shape transformations of nanostructures. However, in the “hot” sites of a SRES substrate, the electric field can be enhanced by 2 orders of magnitude. Consequently, the Joule heating generated in the metal nanostructures can be increased by 4 orders of magnitude and the “hot” sites can be heated by tens of degrees[15] into a temperature range capable of inducing morphological changes in metal nanostructures. In this work, we demonstrate morphological changes of the “hot” site experimentally, an observation that was occasionally made in gap-mode TERS measurements.

In previous research on the blinking phenomenon in SERS measurements, attempts have been made to probe morphological changes and to deduce how these affect the Raman enhancement of isolated Ag particles.[16] A combined system of an atomic force microscope (AFM) and micro-Raman system was used to monitor “hot” Ag particles, but no morphological change of isolated Ag particles was observed. This is because the field enhancement generated by isolated silver particles is much lower than that in nanogaps, and consequently, the temperature rise was much lower than that in the case of a real “hot” site. Furthermore, it is impossible for that setup to look into the hot nanogaps, because the AFM tip is too coarse to resolve these structures.

However, the above difficulties can be overcome by a gap-mode TERS setup, because of its intrinsic capacity for both creating and investigating a “hot” nanogap. In gap-mode TERS, an ultrasharp Ag tip is brought to the surface of a metal substrate to create a “hot” nanogap, in which the Raman spectra can be enhanced by $\sim 10^7$ times, enough for single molecule detection.[2] The same tip can then be employed to scan over the substrate and generate topographic images, which are a convolution between the tip shape and the morphology of the Au surface. If the tip shape or the substrate morphology changes, it will be revealed in the topographic images, with subnanometer precision. With the help of this technique, morphological changes in a “hot” gap and their relation to the irreversible Raman signal losses can be investigated simultaneously.

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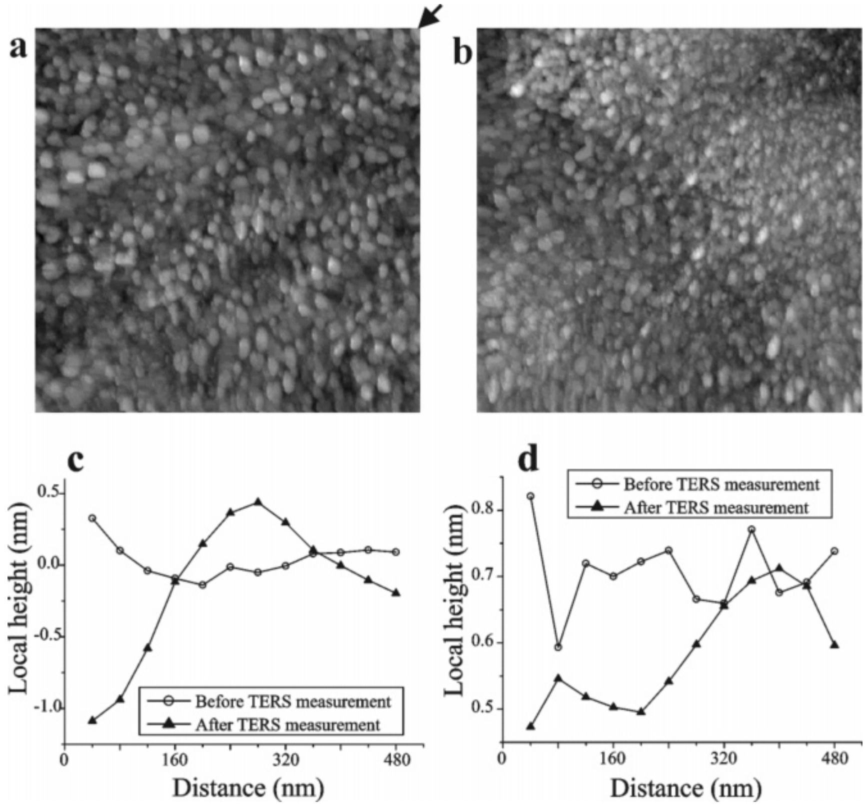

Figure 1. Morphological changes of a "hot" site. Panels a and b are the STM images before and after 1 min of TERS measurement at the upper right corner of the image marked by an arrow. The power of the laser was 1 mW. The size of the scanned area was 500 nm × 500 nm. The mean height and roughness in arc areas with different distances from the "hot" site were calculated and plotted in c and d. Raw data without any preprocessing was used in the calculations.

Experimental Section

The setup of the gap-mode TERS used in this work includes two parts, a scanning tunneling microscope (Nanosurf) and a home-built micro-Raman microscope. The 633 nm laser line of a He–Ne laser was used as the excitation source. The detailed description can be found in our previous work.[2] The Ag tips used in this experiment were made by electrochemical etching. With proper parameters, the radius of curvature of the tip apex can be controlled to 25 nm or smaller. The drift of the tip was suppressed to less than 5 nm in 10 min during the measurements, by shortening the tip and by a long-term prescanning.[17] A low drift is important for the reliability of our data.

The samples used in this work were Au films coated with a benzenethiol monolayer. The Au films were made by vapor coating 100 nm of Au onto freshly cleaved mica substrates and then kept at ambient temperatures without any postannealing. The monolayers were formed by soaking the Au films in a benzenethiol solution with a concentration of 10^{-2} M for 3–4 min. Benzenethiol was chosen because it is relatively stable compared with dye molecules and can form a homogeneous monolayer on Au surfaces. These characteristics are important for us to collect reliable reference data for estimating the field enhancement.

In practice, the morphological changes in the "hot" spots were investigated in the following way. First, a sample area was repeatedly scanned to make sure that the system was stable. Then, the tip was moved to a desired location in the topographic image and a TERS measurement was performed with an excitation laser power of ~1 mW. After that, the topographic image was collected again at the same position to check whether any morphological changes occurred in the "hot" site. The TERS measurement and the subsequent topography scan were sometimes repeated several times until the Raman signal could no longer be observed. In the last step, the activity of the tip was checked by measuring the TERS signal in new sample positions.

Results and Discussion

Near-Field Annealing. Parts a and b of Figure 1 demonstrate one of the most pronounced observations of the annealing effect in the "hot" spots. Before the TERS measurement, the Au surface was homogeneously coved by grainlike structures. After a 1 min TERS measurement, the size of the grains in the vicinity of the measured spot significantly decreased, while farther away from the "hot" spot, the grain size was almost unchanged.

We employed two statistical quantities, local height (i.e., mean of the *z* value of the topography images) and local roughness (i.e., the root-mean square) to characterize the morphological changes. Parts c and d of Figure 1 show the results. A crater structure is revealed by the local height vs distance plot. It appears that the material under the tip was ablated and redeposited 100–300 nm from the "hot" site. The roughness vs distance plot demonstrates a significant distance-dependent roughness reduction effect. At the bottom of the crater, the roughness dropped by 50%, while the roughness outside the crater is much larger. In other words, the Au surface under the tip was annealed.

This annealing phenomenon is a near-field effect because no morphological change was observed with the tip retracted 100 nm from the Au surface. From prior work with gap-mode TERS, it is known that the electromagnetic field can only be highly enhanced when the tip–sample distance is smaller than 30 nm.[2,18] Therefore, the morphological changes are related to the field enhancement in the gap.

It is important to note that the observed topography images are a convolution between the shape of the tip and the Au substrate. Thus, we cannot rule out a change of the tip shape during the measurement. However, the data in Figure 1 proves that it was the morphology of the Au surface that changed during the TERS measurement, because a change in the shape of the tip could not induce a crater structure in the topography. Another piece of evidence for the morphological change of the Au film is that the roughness relaxation is localized at the point of the TERS measurement. If only the tip had changed its shape, only the overall roughness would be changed.

Thermal Effects Lead to the Morphological Changes. There are two possible origins for the light-driven morphological changes: direct field promoted surface diffusion (nonthermal effects) and thermal effects caused by the highly enhanced electromagnetic field in the "hot" spots.

Nonthermal mechanisms have been studied theoretically by Lukatsky et al.[19] They discussed the effects of the external electromagnetic field on the surface tension and the surface diffusion constant, which determine the rate of the surface roughness relaxation. The results predicted that the magnitude of the laser-induced surface tension is more than 11 orders smaller than the value without the external field and can be neglected. Something similar also applies to the diffusion constant, which can be estimated by a linear equation: $D_s = D_s(0)(1 + W^2)$. Here, D_s is the diffusion constant, $D_s(0)$ is the diffusion constant without external electric field, $W \equiv eE_0a/(4k_BT)$, where E_0 is the external electric field, a denotes the diameter of one atom, k_B, is the Boltzmann constant, and T is the temperature. In our case, W is less than 10^{-6}, and consequently, the change of the diffusion constant can be neglected.

Thermal effects induced by localized plasmon resonances are well-known and have been applied to many areas, such as far-field detection,[20] thermotherapy,[21] material sciences,[22] etc. In particular, Elfick and co-workers recently predicted that in TERS experiments, the temperature of the sample could increase by tens of degrees,[15] which is high enough to trigger structural changes of nanoparticles.

To estimate the temperature rise in the "hot" gap in this work, a 3-D stationary model was built and simulations based on our experimental parameters were run using a commercial finite element method solver, *Comsol Multiphysics* (www.comsol.com). Since the field enhancement is localized in the tip−sample gap, we assumed that all the Joule heat is generated in a small volume that includes the tip end and a small part of the sample under the tip apex. The size of the heat source is given by the radius of the tip apex and the penetration depth of the light into Au, which are ~25 and ~28 nm, respectively. The intensity of the incident light is 1 mW/μm^2. The electric field intensity in the tip−sample gap is enhanced by a factor of ~55 according to the experimental data of Raman enhancement.[2] The field intensities in the Ag tip and Au substrate are hence derived by the boundary conditions at the air/metal interfaces. The values of the thermal conductivity and heat capacity of Ag and Au used in the simulation are adopted from the Materials/Coefficients Library of *Comsol Multiphysics* and are 429 and 317 W/(m·K) and 235 and 129 (J/kg·K), respectively. Considering that the heat dissipation through the Au−mica interface was negligible compared with that through the Au film itself, the sample was approximated by an isolated film with the lower boundary thermally insulated. The model was numerically solved by the finite element method solver provided by *Comsol Multiphysics*. The convective heat transfer was also taken into account in this model by an empirical approach, the heat-transfer coefficient method, which is a built-in method in *Comsol Multiphysics*. Figure 2 illustrates the result, showing that the local temperature rise can be more than 30 °C at the tip end, and about 17 °C on the Au film. These values are much lower than the result predicted by Downes et al.,[15] but one should note that this result was obtained by using a conservative estimation of the field enhancement. The real temperature rise can be higher. Semin et al. demonstrated that the shape of Ag nanostructures can be irreversibly changed after minutes of annealing at 35 °C, just 12 °C above room temperature.[23] Combined with the fact that the contribution of nonthermal effects to the morphological changes can be neglected, we conclude that the heating effect is the main reason triggering the morphological changes of the Au surface in this work.

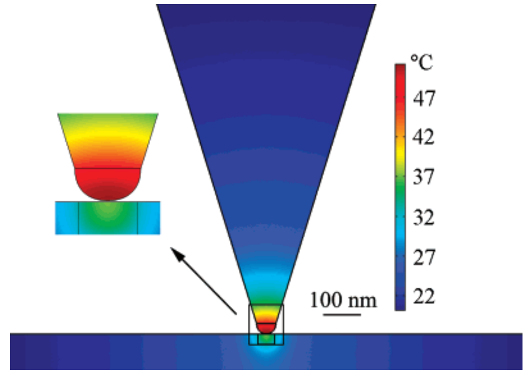

Figure 2. Temperature distribution at the tip−sample gap, simulated by using *Comsol Multiphysics*. All parameters (i.e., field intensity, geometry, etc.) used in the simulation are based on the experiments. The inset shows a zoomed view of the tip apex.

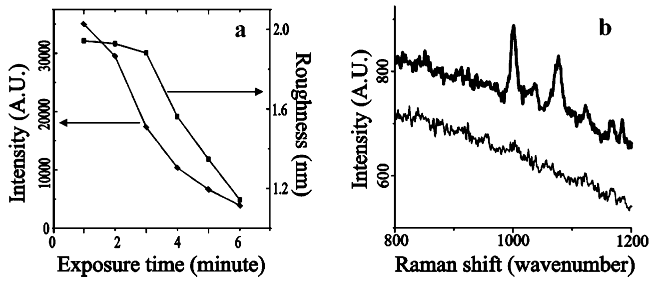

Figure 3. Panel a is an example of how the Raman signal and the local roughness at a "hot" site decrease simultaneously. The topographical data from an 80 nm × 80 nm area around the "hot" site was used to evaluate the roughness. The spectral intensity was calculated by integrating the peak at 1000 cm^{-1}, after subtraction of the broad spectral background. Panel b shows that the tip was still TERS active after the TERS signal was lost at one location. The curve drawn by a light line is the spectrum of the last measurement in the panel a. The curve by a bold line is the spectrum collected at a new position.

To confirm the hypothesis above, we also repeated the same experiments on a crystalline Au surface made by flame annealing with butane flame. No observable morphological changes were observed. This is consistent with the fact that a crystalline Au surface is thermally more stable than that of amorphous Au and provides additional evidence for the heating effect in the "hot" sites.

Irreversible Signal Losses. Irreversible TERS signal losses were always observed accompanying the near-field annealing phenomenon in our experiments. Figure 3a shows a typical example. The Raman signal disappeared after an illumination time of only 5 min. At the same time, the local roughness of

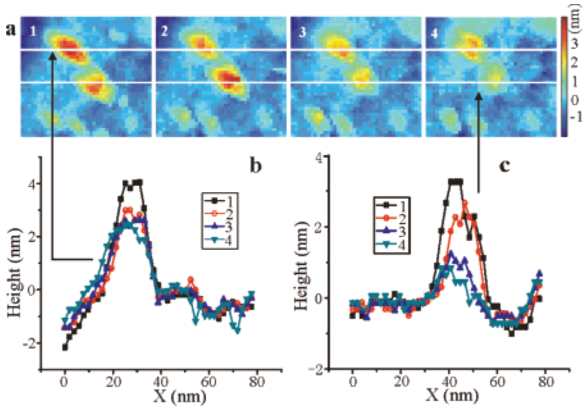

Figure 4. Morphological changes of two isolated protrusions on the Au substrate. A series of topography images is shown in panel a. Between two adjacent images, the tip−sample gap was illuminated by a 1 mW laser beam for 1 min. The cross sections of the two protrusions, which are labeled in panel a, are plotted in b and c.

the “hot” site significantly decreased. In prior studies, several mechanisms had been suggested for the origin of the signal instability in a “hot” site, namely, the desorption and surface diffusion of the adsorbates away from the “hot” site,[24] the decomposition of the adsorbate, and the loss of the chemical enhancement due to the change of adsorption geometry of adsorbates on the Au surface.[6] The analyte used in this work is benzenethiol, which is stable under the irradiation of visible light at a moderate temperature. Thus, the possibility of decomposition can be excluded. Here, we do not need to take into account the loss of chemical enhancement either, because the TERS signal is primarily introduced by the electromagnetic field enhancement. Considering the rapid degradation of the “hot” site, we therefore propose that the reduction of the electric field enhancement due to the roughness relaxation on the metal substrate is one of the main reasons for the irreversible signal losses.

It has been demonstrated recently that the enhancement of TERS is strongly dependent on the local roughness of the metal substrate. A step with a height of 2 nm can increase the local Raman signal by 1 order of magnitude.[17] In Figures 1 and 3, the local roughness is found to decrease only by several angstroms following an exposure of a few minutes, too small of a change to influence the electromagnetic field enhancement in the “hot” site. However, the roughness used here is a statistical value obtained by averaging the local height fluctuations in one area. The morphological change of a single structure on the Au surface is much larger.

In order to quantify the amplitude of the morphological change of individual nanostructures on the Au film, two isolated nanoprotrusions were investigated. Their shape evolution during the TERS measurement is shown in Figure 4a. The height of these grains continuously decreased during the measurement. Their height decreased by 2 nm after an exposure of only 4 min, enough time to cause a considerable change of the local field enhancement in the “hot” site. It is worth emphasizing that the height measurement by scanning tunneling microscopy (STM) is reliable, even if the tip shape changes during the measurement. Thus, the height changes observed in Figure 4 also provide additional evidence for the conclusion that the morphology of the Au surfaces was changed during the TERS measurements.

Further evidence comes from the change of the Ag tip, which, together with the Au substrate, forms the “hot” gap. During the TERS measurements, some Ag tips lost their TERS activity within just a few minutes, implying a change of the tip shape. We can exclude the possibility of oxidation of the Ag tip, because most tips stayed active when exposed for more than 1 h. Moreover, the mechanical damage of the Ag tips was not likely, either, because the feedback of the STM was reliable and no change in the topography images was observed without exposing the sample to the laser. Therefore, it must have been the heating effect causing the shape change of the Ag tips. This is also consistent with the simulation result that the temperature rise at the tip apex is higher than that of the Au surface. On the basis of the discussion above, we propose that the morphological change of the “hot” gap (including the shape changes of both the Au substrate and the Ag tip) can cause irreversible signal losses.

It is necessary to point out that the change of the tip shape is not a real problem for TERS, because the tip shape will stabilize after exposure to the laser for the first several minutes. Figure 4 provides proof of this argument. The structural change of the nanoprotrusions was much more significant in the first 2 min than that later on. In other words, if a tip maintains its TERS activity after the first exposure, it will be stable for a much longer time.

Besides the degradation of the “hot” gap, surface diffusion of adsorbates or even adsorbate desorption can also lead to signal loss. Figure 1 shows that some Au atoms moved away from the “hot” site during a TERS measurement. The benzenethiol molecules, which are bound to the Au surface, are likely to migrate out of the “hot” site at the same time. We cannot observe any diffusion of benzenethiol molecules with the STM directly, i.e., it cannot be proven that the adsorbates are indeed removed from the “hot” site. Adsorbate desorption appears to be less likely than loss of TERS activity due to annealing, because the tips were rarely found to be contaminated during a measurement. If molecules desorb from the Au surface, they should easily be able to redeposit on the surface of the Ag tips and cause tip contamination. Another argument is that the desorption of a thiol molecule from an Au surface requires a temperature of 150 °C, much higher than the simulated temperature.[25]

Finally, we would also like to mention that this near-field annealing phenomenon only happened to a small portion of the tips (<10%). In most cases, no topography change was observed. This is interesting because it shows the possibility of producing robust “hot” sites, one of the most crucial issues for developing robust SERS-based sensors. So far, all the studies imply that the local temperature rise in the “hot” sites is the reason for the roughness relaxation. From this point of view, two key issues in the design of a robust “hot” site will be good heat-dissipating capacity and resistance to high temperature.

Conclusions

In summary, a near-field annealing phenomenon was observed in TERS experiments. The local roughness at the “hot” spot was significantly decreased after only minutes of laser illumination. We propose that this phenomenon is triggered by thermal effects, which are supported by simulations. We also investigated the relation between the losses of the TERS signal and the morphological changes. The results suggest that the amplitude of the roughness relaxation in the “hot” gap is large enough to cause an observable loss of electromagnetic field enhancement. This provides us with a new explanation for the signal instability observed in the hot nanogaps during SERS and TERS experiments.

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