

## Tip-enhanced Raman spectroscopy for investigating adsorbed species on a single-crystal surface using electrochemically prepared Au tips

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(Received 4 February 2007; accepted 7 August 2007; published online 4 September 2007)

A tip-enhanced Raman instrument was set up based on a homemade optical fiber Raman head, a dispersive spectrograph, and a scanning tunneling microscope (STM) system. Electrochemical preparation of tip-enhanced Raman spectroscopy (TERS) Au tips was refined by using the etching current as ending point control, resulting in a success rate as high as 90%. The high quality Au tips allow the recording of STM images with molecular resolution and TERS spectra of nonresonant surface species on a single-crystal surface. © 2007 American Institute of Physics.

[DOI: 10.1063/1.2776860]

Apertureless scanning near-field microscopy has witnessed a great surge in recent years after the first reports on the realization of tip-enhanced Raman spectroscopy (TERS),<sup>1–4</sup> which leads to the generation of the family of tip-enhanced optical spectroscopy.<sup>5–10</sup> The use of metallic Au or Ag tips that support the excitation of localized surface plasmon resonance in the visible to near-infrared light regions provides unprecedented opportunities to physicists, chemists, and spectroscopists to investigate with improved surface detection sensitivity up to 6 orders of magnitude for detecting several molecules or even single molecule,<sup>11–13</sup> spatial resolution as high as 14 nm,<sup>14,15</sup> and abundant chemical signatures.<sup>16–18</sup> Several years after the first experimental report of TERS, there are still continuous efforts to design TERS instruments<sup>19–24</sup> and propose different tip-preparation methods,<sup>1,14,16,25,26</sup> indicating that TERS is still a growing technique and is still far from maturity. Up to now, there is no TERS report on obtaining scanning tunneling microscopic (STM) images with molecular details of the sample in order to correlate the morphological and spectral information. In fact, in most of the reported TERS results, atomic force microscope (AFM) or tuning fork scanning force microscope (SFM) were used; therefore, the spatial resolution cannot reach the atomic resolution. On the other hand, the preparation of TERS tip generally borrows the sophisticated methods discovered for preparing SPM tips. Due to the different requirements for the TERS and the SPM tips, there is still huge effort to obtain nice and reproducible TERS tips, in terms of achieving a better preparation efficiency, maximal TERS enhancement, and reproducibility in TERS measurements.

In the present letter, we set up a tip-enhanced Raman instrument and refined the preparation of Au tips by electrochemical etching methods, which allow us to obtain STM images with molecular resolution and TERS spectra of nonresonant surface species on a single-crystal surface.

Figure 1 shows the schematic diagram of a homemade optical fiber head. The laser is coupled to an optical fiber head by an optical fiber and collimated into a parallel beam

that then passes through a plasma line filter to reject the plasma lines and the fluorescence signals generated inside the fiber to give a monochromatic laser line. The laser power can be adjusted by selecting a proper grade of neutral density filter to suit the experimental requirement. The laser is then reflected by a mirror and a notch filter and focused on the sample surface by a microscope objective. The optical signal produced on the sample is then collected by the same objective in a backscattering mode. In the collected signal, a major portion of the reflected laser light and Rayleigh scattering is rejected by the same notch filter, and the spectral signal away from the laser wavelength can pass the notch filter, be focused into the collection fiber, and then be transmitted to the spectrometer for detection.

In a tip-enhanced Raman study, it is important to precisely focus the laser into the gap of the tip and sample. For this purpose, independent of the laser pathway, a white-light imaging path was designed. The white light is collimated into a semiparallel beam, reflected by a beam splitter, and is illuminated on the sample surface by the objective. The image of the sample is collected by the same objective, reflected by the second beam splitter, and focused onto a charge coupled device video camera by a properly designed convex lens to produce a clear optical image that is then displayed on a monitor. The total size of this optical fiber head is only about 16(L) cm × 10.5(W) cm × 7.3(H) cm. This design allows a convenient coupling of this head with any commercialized spectrographs with optical fiber adaptor

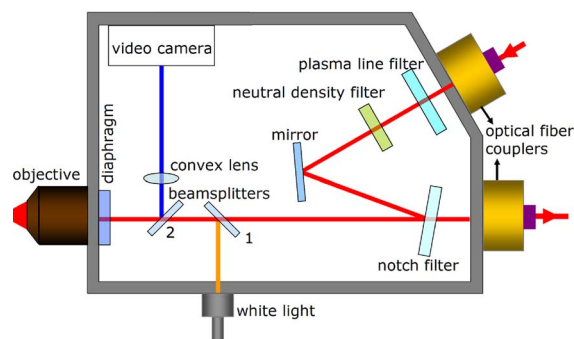


FIG. 1. (Color online) A schematic diagram of a home made optical fiber head.

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available. Because the size of the head is very small, it can be installed in upright, epi-, and tilt-reflection modes and coupled with various SPM systems. Furthermore, since the base of the head was machined from a whole piece of aluminum, it is sufficiently rigid to resist any optical misalignment due to the slight environment change.

Beside the proper design of the TERS instrument, it is equally important to fabricate a nice TERS tip to obtain STM images of high spatial resolution and observable TERS signal. There are two prerequisites on the quality of a TERS tip: (1) The tip should have a very sharp tip apex, ideally only one atom, for STM imaging with high spatial resolution; and (2) it should have a smooth surface and nice tip shape to produce enhanced electromagnetic field localized around the tip apex. It should be noted that even after several years' development of TERS, how to produce TERS tips with high quality and reproducibility is still a central problem bothering most TERS scientists. Therefore, it is not surprising that at the SM-SERS and TERS symposium held in Tsukuba in 2006, the concluding remark is "tip, tip, and tip!!!"

In 2004, we proposed a method to electrochemically etch Au tips in a mixture of fuming HCl and ethanol and used them to obtain TERS signal.<sup>27</sup> However, it was difficult to find tips that are capable of obtaining high-resolution STM images with a relatively high success rate. The main problem is that we determined the end point of the etching process by naked eyes, which inevitably leads to over etching of the tip. Furthermore, to ensure the quality of the tip, the tip had to be characterized with scanning electron microscope (SEM), which might inevitably contaminate the tip with carbonaceous species during exposure in air and in SEM instrument. In this letter, we made further improvements over the previous method.

The Au tip was prepared by immersing a 12-mm-long Au wire (about 2 mm immersed in the solution) with a diameter of 0.25 mm in the etching solution at the center of a large Au ring merely immersed in the solution. The Au wire and Au ring served as the anode and cathode, respectively. A potentiostat was used to keep the potential applied on the wire at exactly the preset value. The previously used etching voltage of 2.4 V roughly corresponds to 2.2 V when a potentiostat is used. Furthermore, with a potentiostat, we can now monitor the electrochemical current response during the etching process and set optimal current value to terminate the etching process, which can solve the over-etching problem completely.<sup>28</sup>

It has been found that the etching process of Au in HCl is accompanied by a current oscillation process due to the passivation and activation of Au surface by the formation and dissolution of AuCl film.<sup>27</sup> The upper row of Fig. 2 shows the typical current response during the etching process. It can be seen that the current response is the most stable and occurs throughout the etching process when the voltage is about 2.2 V. When the etching voltage becomes higher, the etching process cannot be sustained with an oscillation between low and high currents leading to an extended etching time. When the etching voltage is low, the current oscillation can only be initiated after some etching time, leading also to an extended etching time. We further noticed a trend that with the increase of etching voltage, the tip becomes slim and the surface roughness also increases, which is not good for both the STM imaging and TERS study. Comparing Fig. 2(a) with Fig. 2(b), we find a very

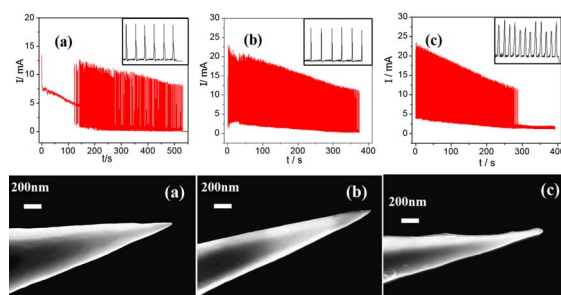


FIG. 2. (Color online) Top panel: current time curves of Au wires etched in a mixture of HCl:ethanol (1:1v/v) at different voltages. Bottom panel: SEM images of the etched Au tips. A: 2.1 V, B: 2.2 V, C: 2.4 V.

interesting phenomenon that when the current oscillating curve presents a good periodicity, the shape of the tip will be nice, which can be used to screen for the quality of the tip without turning to SEM. This measure not only reduces the contamination but also increases the efficiency in the TERS experiment. The success rate in obtaining a TERS-active tip is as high as 90%.

On the basis of the homebuilt TERS instrument and the electrochemically etched Au tip, we obtained tip-enhanced Raman signals and STM images with a molecular resolution from 4,4'-bipyridine (4BPY), a nonresonant molecule monolayer adsorbed on a Au(111) surface. A highly ordered monolayer of 4BPY can be obtained by dropping a droplet of acidic 4BPY solution on a preheated Au(111) surface. The STM image obtained in air with a clean Au tip is given in Fig. 3(a) and the high resolution image obtained with Pt-Ir tip is also given as the inset of Fig. 3(a) for clarity. The simulated model shows the unit cell with parameters of  $a = 0.8 \pm 0.1$  nm and  $b = 1.0 \pm 0.1$  nm, which agrees well with the result of Diao *et al.* of a flat-lying 4BPY.<sup>29</sup> This result indicates that 4BPY forms the ordered structure with the ring plane parallel to the surface. The fact that the N atoms in the 4BPY molecules are negatively charged implies that there must be some other positive species, e.g., proton, acting as a bridge to pair two 4BPY molecules. By statistics, we found that about 50% of the electrochemically etching Au tips were capable of obtaining STM images with a molecular resolution. The corresponding Raman spectra are shown in Fig. 3(b). The bottom line in Fig. 3(b) corresponds to the condition that the tip was out of the tunneling region. As expected, there is no detectable signal from the monolayer species by conventional confocal Raman spectroscopy.<sup>12</sup> However, when the tip approached the substrate within the tunneling distance, a very nice Raman signal from the surface was detected, even with a laser power of 1 mW. In the TERS spectrum, the four peaks at 1015, 1220, 1293, and 1607  $\text{cm}^{-1}$  are the characteristic bands of 4BPY, assigned to ring stretching and C-H in-plane-bending modes with  $a_1$  symmetry.<sup>30</sup> However, a strong band at 238  $\text{cm}^{-1}$  and a shoulder band at 1635  $\text{cm}^{-1}$  were also detected. These two bands could not be detected in the surface-enhanced Raman spectroscopic (SERS) measurement in the acidic 4BPY solution, using Au nanoparticles as the SERS substrate; see top spectrum in Fig. 3(b). The 1635  $\text{cm}^{-1}$  band exists in the normal Raman spectra of solid 4BPY and the protonated 4BPY solution. In both cases, the two N atoms in 4BPY are connected with other N atoms in crystal structures or with the protons in highly acidic solution. The latter is in agreement with the STM result. Meanwhile, the band at 238  $\text{cm}^{-1}$  that cannot be ob-

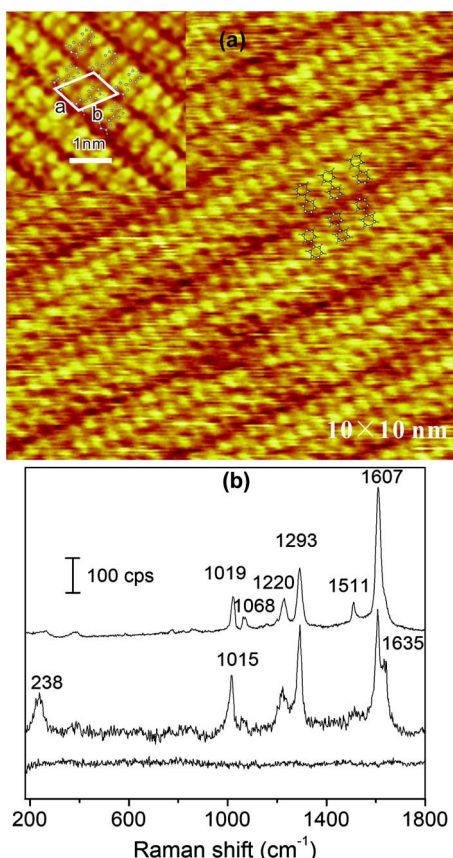


FIG. 3. (Color online) (a) STM image ( $10 \times 10 \text{ nm}^2$ ) of 4,4'-bipyridine adlayer on a Au (111) surface obtained with a Au tip (inset shows the high resolution STM image obtained with a Pt-Ir tip). The position of the molecules on the image is indicated by the chemical structure of 4,4'-bipyridine. The bias potential of the tip and the tunneling current were 80 mV and 1.0 nA, respectively. (b) TERS spectra for the 4,4'-bipyridine SAM layer on the Au(111) surface (middle spectrum), the bottom spectrum for the tip-retracted case, and the top spectrum for the SERS spectrum. Acquisition time: 100 s. Laser power: 1 mW.

served in both SERS spectrum and normal Raman spectrum is believed to arise from the phonon vibration of the highly ordered monolayer structures. It should be especially pointed out that the contamination of the tip can be convincingly excluded in the present study.

In TERS spectrum, the bands that we detected all belong to the  $a_1$  symmetry. It seems as if 4BPY is adsorbed perpendicularly to the surface. The above analysis of STM result and that of Diao *et al.* pointed out that the 4BPY molecule is adsorbed flatly on the surface.<sup>29</sup> Surface selection rules of Raman spectroscopy points out that for a molecule with  $C_{2v}$  symmetry, such as 4BPY, the orientation of the molecule on the surface can be determined by considering the relative enhancement of  $a_1$ ,  $a_2$ ,  $b_1$ , and  $b_2$  modes, by comparing the related mode in SERS or TERS spectra with that of free molecules.<sup>31</sup> However, in the present case, it is still difficult to use this selection rule to figure out the orientation of molecules on the surface, due at least to the following two reasons: (1) it is very difficult to obtain both the solution and TERS spectra with sufficient signal to noise ratio for those modes other than  $a_1$  modes, and (2) the surface plasmon resonance frequency of the tip-sample configuration in TERS is still difficult to be measured. Therefore, although what we obtained is the  $a_1$  modes, it is still not conclusive whether the

molecules are adsorbed on the surface via a flat or vertical orientation. However, the simultaneously obtained STM image at the same location points out that the molecules may be adsorbed on the surface in a flat orientation.

In conclusion, we have obtained reasonably good tip-enhanced Raman signal and molecular resolution STM image of the ordered monolayer 4BPY on the Au(111) surface on the homemade tip-enhanced Raman instrument with electrochemically prepared Au tips, which allows us to propose that the 4,4'-bipyridine molecules may be adsorbed flat on the surface.

This work was supported by the NSFC (20473067 and 20673086), MOE (20040384010 and NCET-05-0564), FYT (101015) and 973 program (2007CB935603).

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