THE JOURNAL OF PHYSICAL CHEMISTRY B LETTERS

2005, *109,* 16571−16574

Published on Web 08/13/2005

SERS and Tunneling Spectroscopy Investigation of Iron-Protoporphyrin IX Adsorbed on a Silver Tip

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Received: July 19, 2005; In Final Form: August 8, 2005

Iron-protoporphyrin IX adsorbed on a scanning tunneling microscopy silver tip is investigated by combining surface enhancement Raman (SERS) and tunneling spectroscopies down to single molecule regime. Both the Raman signals and the tunneling current intensity reveal fast switching between the iron oxidation states and present analogous, significant fluctuations in time. The results point out the occurrence of a strong electronic coupling between the molecule and the metal, and may contribute to elucidate the dynamical phenomena at the molecule−metal interface, deserving some nanotechnological interest.

The study of organic molecules in the proximity of metal surfaces has gained a new interest in the perspective of building hybrid nanodevices and light-harvesting systems.[1−3] Indeed, the capability of some molecules to perform specific functions, such as electron transfer (ET), light emission, catalysis, etc., can be combined with processing power of microelectronics for the realization of nanosensors and nanodevices, even working in the single-molecule limit.[4] However, a molecule directly adsorbed on a metal surface undergoes multiple interactions and drastic changes in its optical and conductive properties might take place.[5−7]

Molecules on nanostructured metal surfaces (colloidal particles, rough metal electrodes, etc.) revealed a huge Raman signal enhancement, leading even to single molecule detection;[8−13] this being at the basis of surface enhancement Raman spectroscopy (SERS).[5,14] Together with an electromagnetic (EM) effect, responsible for the local field enhancement involving surface plasmon resonance, a charge transfer (CT) between the molecule and the metal surface has been suggested to contribute to SERS.[15−17] The CT effect, which requires a chemical interaction between the molecule and the metal surface, might involve a reversible ET between them, as recently suggested by a single-molecule SERS study.[18] Conversely, injection of electrons by a silver tip in scanning tunneling microscopy (STM) single molecule experiment can induce photon emission and the vibrational modes of a porphyrin molecule adsorbed on a conductive substrate have been probed.[19]

We have, therefore, performed a SERS/STM combined experiments in which an organic molecule has been adsorbed on a silver STM tip whose roughness is suitable to hugely enhance the molecule vibrational spectral emission at the level of single molecule. Furthermore, we have investigated the electron flow in the molecule−tip tunneling junction, mounted in STM equipment with the same geometry used for the SERS experiment. We have focused our attention on the iron-protoporphyrin IX (FePP) organic molecule, whose vibrational and conductive properties have been well characterized separately by both SERS and STM.[20−22]

On one hand, the study of the FePP−tip system can provide some insight on the SERS mechanisms; on the other, it could offer the possibility to better elucidate the dynamical and spectroscopic properties of molecules at metal surfaces. In the present case, particular attention has been devoted to investigate the fluctuations occurring in both the SERS and tunneling current signals when the single-molecule regime is approached.

Fe−PP (Sigma, purity higher than 98%) was dissolved into a KOH solution 0.1 M at pH = 12 at a concentration of 10^{-6} M; solutions at lower concentrations were obtained by successive dilutions. Absorption spectrum of FePP in KOH is consistent with a ferric oxidation state.

Silver STM tips, prepared by cutting a silver wire, were washed in acetone, ethanol, rinsed in ultrapure water, and incubated for 1 h at room temperature with an FePP solution at 10^{-9} M. The SERS spectra were recorded by a Labram confocal system (Jobin-Yvon) equipped with a Peltier-cooled CCD detector and with a 100× microscope objective with NA = 0.9, and confocally coupled to a 300 mm focal length spectrograph with a 1800 grooves/mm grating.

Tunneling spectroscopy (TS) was performed with a PicoSPM (Molecular Imaging). $I-V$ curves were recorded on FePP adsorbed on silver tips in close proximity of a freshly cleaved highly oriented pyrolitic graphite electrode (HOPG) and by temporarily disengaging the piezo feedback loop in a nitrogen atmosphere. The scan was disabled and the tip set at a tunneling resistance of 4×10^{10} Ω (200 mV, 5 pA). The STM feedback was opened and the bias scanned from −1 to +1 V, with sweep duration of 0.1−0.3 s, being the servo control restored at the end of each sweep.

An analysis of the SERS signals detected in sequence, from a silver tip incubated with FePP at 10^{-9} M, has revealed drastic and rapid intensity and spectral fluctuations. Lines appear and disappear suddenly, and the relative peak intensity, as well as the frequency of the lines, changes in time. Figure 1A shows

10.1021/jp053979p CCC: $30.25

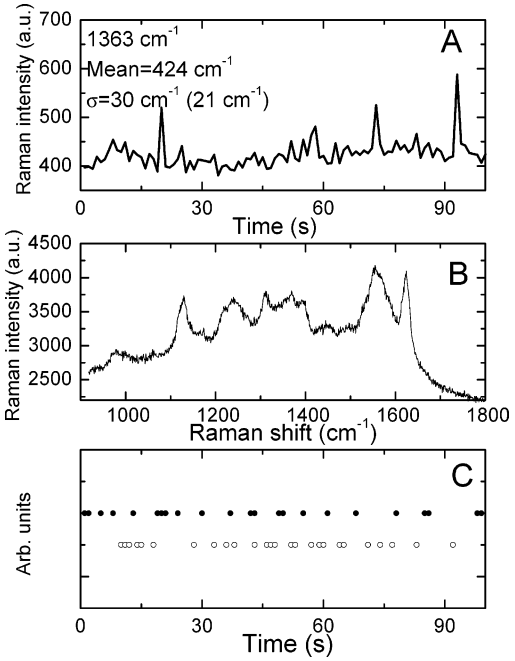

Figure 1. (A) Raman intensity detected at 1363 cm^{-1}, as a function of time, from a silver tip incubated with FePP in single-molecule regime. The mean and the standard deviation values, together with the expected value from noise, are shown. (B) Spectrum as derived by collecting all the SERS spectra detected in the temporal sequence. (C) Appearance of Raman peaks as a function of time at 1363 cm^{-1}, ferrous state, (full circles) and 1375 cm^{-1}, ferric state (empty circles). A peak is detected when the corresponding intensity overcomes a fixed threshold (above 2σ of the background level). SERS measurements have been performed by putting the tip in vertical position with its overall surface inside the laser spot toward the microscope objective; each spectrum having been obtained with 1 s of integration time. The spectral resolution is lower than 5 cm^{-1}. The laser spot size is about 1 μm in diameter.

the intensity of the 1363 cm^{-1} line as a function of the recording time. Such a frequency corresponds to the vibrational marker of the ferrous iron state, and the behavior of this line should be considered as representative of all the other lines investigated, its intensity varying rapidly in time, similar to what has been previously observed.[13,18,20] Notably, the standard deviation extracted from the temporal trend of this representative line (see the values in Figure 1A) exceeds that expected from the background noise (see value in parentheses in Figure 1A). As amply stated in several works (see for example refs. 8, 10, 11, 13, and 18), the presence of drastic fluctuations, together with the extremely low iron-protoprophyrin IX concentration, constitutes a hallmark for the fact that single molecule detection has been reached. We remark additionally that the main vibrational features of FePP can be recovered when several spectra are summed (see the spectrum in Figure 1B).[23]

By following the procedure reported in ref 19, we have analyzed the temporal appearance and disappearance of the vibrational peaks at 1363 and 1375 cm^{-1}, corresponding to the vibrational markers of the ferrous and ferric iron states, respectively. In a sequence of 100 spectra (each one taken in one second), peaks at both 1363 cm^{-1} (full circles in Figure 1C) and 1375 cm^{-1} (empty circles in Figure 1C) have been randomly and alternatively detected as a function of time. Such a behavior, already observed for FePP on silver colloids,[18] can be put into relationship to fast and reversible changes in the oxidation state of the FePP iron ion during the measurements. An ET process can be invoked; accordingly the molecule could undergo a nonradiative process where ballistic electrons from the silver surface could jump toward the FePP molecule and backward.[24] Therefore, even if we cannot exclude that interfacial molecule−metal interactions might assist such an ET process, it could be quite reasonable that the energy required to overcome the barrier between the two oxidation states could be provided by light excitation.[4]

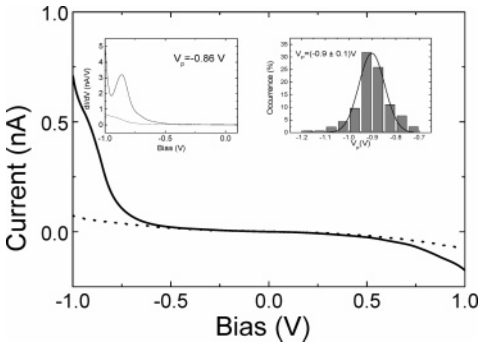

Figure 2. $I-V$ characteristics as recorded by tunneling spectroscopy (FePP−tip (solid line) and bare tip (dash line)). Measurements were performed under nitrogen atmosphere at starting tunneling resistance of 4×10^{10} Ω (bias, 0.2 V; tunneling current, 5 pA). (left inset) Numerical derivative dI/dV. (right inset) Distribution of peak potentials as detected from dI/dV plots of different FePP−tip systems. Solid line is a Gaussian fit. Each single $I-V$ spectrum consists of the average over 100 consecutive bias sweeps.

By repeating the measurements on different tips incubated with FePP, different intensity trends in time have been obtained, but the overall features have been maintained. Tips incubated with the same buffer solutions but without FePP do not reveal any Raman signals over the noise. In a few cases, the detected Raman signal was dominated by two characteristic peaks, at 1350 and 1580 cm^{-1}, usually attributed to carbon contamination.[7,25] These samples have been discarded.

The observed changes of the iron oxidation state as induced by illumination, are indicative of the presence of a strong electronic coupling between the molecule and the metal. Owing to such a coupling, it would be interesting to investigate the current tunneling properties of the FePP molecule, after having been adsorbed on an STM tip and forming a tunneling junction when brought against a HPOG substrate. The recorded $I-V$ curve is shown in Figure 2 (continuous line) together with data related to a bare tip (dashed line). The tunneling current as function of bias in the presence of FePP appears markedly asymmetric, increasing rapidly up to about 0.8 nA for negative bias lower than −0.7 V, while it remains small in reverse bias. At variance, the tunneling curve for the bare silver tip is highly symmetric, with absolute current intensity smaller than 0.2 nA. Generally, the observed trend for the $I-V$ curve, indicative of diode-like curve (current rectification),[26] reflects the redox properties of the molecule.[21] Quantitative information can be extracted from the derivative dI/dV shown in the inset of Figure 2 for both the FePP−tip and the bare tip. A peak at about V_p= −0.86 V is clearly detected for the FePP−tip, while no peaks are observed for the bare tip (see dashed line in the inset of Figure 2). Such behavior can be interpreted in the framework of the Schmickler theory, from which the extra current results from tunneling via oxidized states on the molecule as the bias voltage is made more negative.[27] Actually, the position of the peak is characteristic of the energy gap from the filled state to the first excited state, likely shifted away by the reorganization energy λ. By taking into account that an energy gap of about 0.4 eV is expected for FePP, a reorganization energy of 0.45 eV can be derived from the detected V_p value, in good agreement with the results from porphyrins.[21,22] By repeating the measurements on different FePP−tip samples, some spread in peak

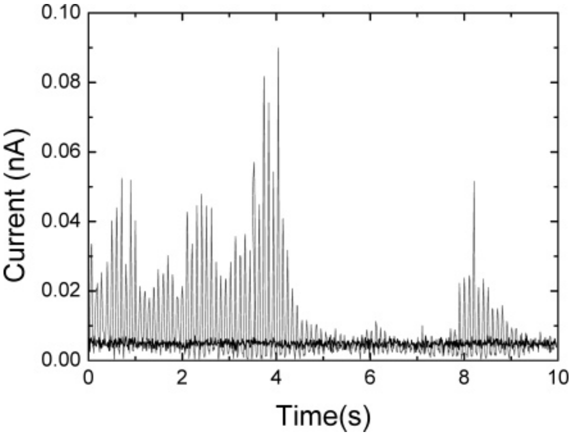

Figure 3. Tunneling current as a function of time time at −0.2 V bias for bare tip (black curve) and for a silver tip incubated with FePP (gray curve).

position of the d*I*/d*V* curves is observed. A statistical analysis performed on 100 FePP−tips has revealed a monomodal distribution well described by a Gaussian, centered at about $V_p = -0.9$ eV and with $\sigma = 0.1$ V (see right inset of Figure 2). Such a variability, similar to that detected in porphyrins adsorbed on noble metal surfaces, can be attributed to tunneling processes modulated by fluctuating local environments.[22] This could also offer a ground to describe the fluctuations appearing in the SERS spectra. Actually, a variability in the arrangement of the molecule on the metal surface may result in a slightly different electronic coupling between the molecule and the metal, affecting thus the sampling of the vibrational modes.

Further information on observed phenomena in the FePP−tip system can be obtained by measuring the tunneling current fluctuations, at fixed bias, as a function of time. The tip has been approached to a HOPG substrate until a preset tunneling current of 5 pA was read at a bias of 0.2 V. The current flowing through the tunneling junction has been recorded in sequence of 10 s at a fix bias of −0.2 V, with the feedback control transiently disabled. While the current recorded on a bare tip is almost constant with very small fluctuations (Figure 3A), on the contrary, the FePP−tip system exhibits drastic tunneling current fluctuations (see Figure 3B). Such behavior, observed for different FePP−tip systems and for different applied bias, is indicative of a significant variability in the tip−molecule−substrate junction occurring during the tunneling experiments.

Our combined SERS and TS study of an FePP molecule adsorbed onto a silver tip has put into evidence fluctuations in time of both the Raman signal and the tunneling current. Generally, these effects could reflect a variety of phenomena occurring at the molecule-metal interface; e.g., the intrinsic dynamics of the molecule, the metal−molecule interactions, likely depending on the specific site at which the molecule is located, etc. More specifically, our results reveal that the temporal fluctuations, at a specific site, are concomitant with an ET between the molecule and the metal. Concerning the SERS experiments, it can be hypothesized that an electron moves from the optically excited molecule LUMO into energetically accessible density of states within the conduction band of the metal.[5] Then, thermally relaxed electrons from the bottom of the conduction band, or from local traps, move to the HOMO of the molecule. In tunneling experiments, electrons move from the conduction band of the tip to the conduction band of the substrate through the LUMO level of the molecule.[22] On such a basis, the observed fluctuations, reflecting a change in the electronic coupling between the molecule and the metal, can be traced back to migrations of the molecule and/or changes of the molecule orientations with respect to the metal surface during the measurements. We remark that porphyrins, characterized by a relatively flexible structure[28] and weakly adsorbed on metal surfaces, may undergo small perturbations or even diffusive processes, through long jumps during the measurements.[29] On the other hand, it has been observed that injection of tunneling electrons by an STM tip on porphyrin molecules can excite its vibrational modes, eventually leading to diffusive processes.[30] This provides some evidence for a coupling between electronic and vibrational properties at the level of single molecule. Therefore, our results could be interpreted in terms of continuous changes of the spatial arrangements of the molecule at the metal interface; such evolution, likely modulated by the particular microenvironment, could affect the ET properties of the molecule.

In summary, this work shows that a silver tip can be used to obtain a SERS enhancement comparable to that achieved from silver colloidal particles. Remarkably, in comparison to other Raman-STM tip-based methods, in which the target molecules are adsorbed on a planar surface and the nanometer-sized tip is brought into an optical contact with the adsorbate,[31−33] our approach may yield a higher SERS enhancement allowing also a contribution from the CT through the molecule−metal contact. Furthermore, the reported approach offers the possibility to simultaneously investigate the vibrational and conductive properties of molecules adsorbed on the metal tip. These aspects could be relevant in the perspective of exploiting organic molecules in the building of hybrid nanodevices.

Acknowledgment. This work has been partially supported by the FIRB-MIUR Project "Molecular Nanodevices" and aPRIN-MIUR 2004 project. Thanks are due to Dr. Dario Alliata for his preliminary STM measurements.

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