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Ultraviolet Raman study of thymine on the Au electrode

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Abstract

We record the potential-dependent Raman spectra of thymine adsorbed on the roughened Au electrode by ultraviolet (UV) excitation at 325 nm, and we find that the surface-enhanced Raman spectra of thymine changed intensely with the negative shift of the applied potential. When the vibrational mode changes, the resonance potential (potential of maximum intensity) varies accordingly, indicating that the thymine molecules were chemisorbed on the roughened Au surface. The charge transfer (CT) mechanism could probably explain the experiment results in the present work.

Keywords: Ultraviolet (UV) Raman; Thymine; Au electrode; Charge transfer (CT) process

1. Introduction

Since the first observation made by Fleischmann et al. [1], surface-enhanced Raman scattering (SERS), with its very high surface sensitivity and selectivity, has become a potentially ideal technique for studying chemical and physical interface phenomena [2–4]. It has been applied as a powerful technique for innovative and extensive analytical applications in surface science, electrochemistry, biology and materials research [5–7]. But we know that the conventional SERS spectroscopy usually works well with the excitation lines from the visible (450 nm) region to the near-infrared (NIR, 1064 nm) region [2–10]; however, there are inherent difficulties in the SERS experiment with ultraviolet (UV) excitation. Because of the experimental limitations, the reports of UV-SERS are very few.

Due to its high energy, UV line could lead to resonant Raman transition or near resonant Raman transition among the electron energy levels, which increases the great sensitivity and acquires more abundant information about the molecule's vibration and structure [11]. Therefore, resonance enhancement can be employed to enhance the Raman signals of some biological molecules selectively in order to reach the low detection limit. Consequently, resonance Raman spectroscopy, especially ultraviolet resonance Raman spectroscopy (UVRRS), has been applied in the biological fields increasingly [12,13]. Moreover, ultraviolet resonance and surface-enhanced Raman effects can be combined together to produce the ultraviolet surface-enhanced resonance Raman spectroscopy (UV-SERRS). Therefore, it is significant to obtain more fruitful data in the UV region and reveal the experimental rule.

As for the proteins and nucleic acids, the surface-enhanced Raman spectra excited by visible light are overlapped, which makes them complicated to analyze. Recently, it has been shown that more information about proteins and DNA (or RNA) can be obtained from the UV resonance Raman spectroscopy [14–20]. Thymine is not only one of the important pyrimidine bases of DNA, but also a frequent model of theoretical studies due to its biochemical importance [21,22]. Though the SERS spectra of thymine have been reported many times [23–28], the excitation lines are all located in the visible region. We obtained the UV-SERS of thymine on the roughen Au electrode for the first time.

In the present work, we studied the UV-SERS of thymine molecules adsorbed onto roughened Au electrode under different electrode potential. The potential-dependent surface Raman spectra of thymine are very different to the UV Raman spectra of thymine aqueous solution both in intensity and in the location of the Raman peaks. Especially with the change of the potential from −0.1 to −1.3 V, the surface Raman spectra changed obviously and when the vibrational mode changes, the resonance potential varies accordingly. Correspondingly, it can be assumed that the variation of SERS intensity as the applied voltage changes is a reflection of the electronic behavior, which was related to the charge transfer mechanism. So, we conclude that thymine molecules are chemisorbed on the Au electrode and

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charge transfer (CT) effect could probably explain the experimental results in the present work.

2. Experimental

Thymine (99% pure) was purchased from Sigma–Aldrich and used without further purification. The UV Raman spectra were recorded with a Renishaw RM2000 micro-spectrophotometer, with a holographic notch filter and a CCD detector. A 15× objective was used to achieve a 180° backward scattering configuration. The excitation source was the 325 nm line of a K3301 R-GHelium–Cadmium laser. The power of laser on the sample was about 3.5 mW. The slit-width was 50 μm and the resolution was 2 cm^{-1}. The optical absorption spectra were measured with a SHIMADZU Model UV-2401 PC UV-visible spectrophotometer.

A three-electrode spectro-electrochemical was used to perform the oxidation–reduction cycles (ORCs). The counter electrode was a platinum ring (99.9%). An Ag/AgCl electrode was used as reference. The working electrode was made from 99.9% polycrystalline gold rod ($\Phi = 3.5$ mm), which was mounted in a Teflon holder. A CHI660A electrochemical instrument was used to control the applied potential of the working electrode. The gold electrode was first mechanically polished with 1.0, 0.3 and 0.05 μm alumina powder in turn to a mirror finish followed by ultrasonic cleaning with Milli-Q water, then it was mounted in the cell filled with 0.1 M KCl solution. The Sweepstep Functions was used. At the roughened surface of Au electrode, 24–25 oxidation–reduction circles were performed with a double potential step: −0. 25 to 1.25 V and kept for 8 s at 1.25 V, then back to −0.25 V and kept for 30 s. Sweep speed was 500 mV/s. When the process was finished, we can see the color of Au electrode surface was dark brown. This ex situ pretreatment was performed to form a relatively stable gold surface, which could sustain a rather constant Raman intensity for measurement. After being subjected to the roughing pretreatment, the electrode was immersed in the spectroelectrochemical cell that was filled with 0.01 M thymine and 0.1 M KCl for measurement. A Raman spectrum was normally measured after keeping the Au electrode at a fixed potential for 2 min, and the potential-dependent Raman spectra were acquired by moving the potential stepwise in the negative direction. All the potentials were quoted versus Ag/AgCl electrode.

3. Results and discussion

By the UV line excitation, the high quality Raman spectrum of thymine aqueous solution (0.005 M) was obtained, as is shown in Fig. 1a. Since the quality of the UV Raman spectrum of thymine aqueous solution is much better than those obtained with NIR and visible excitations, the notable surface-enhanced Raman signal with UV excitation would be desired. In Fig. 1, the UV surface-enhanced Raman spectrum of 0.01 M thymine aqueous solution in 0.1 M KCl on the roughed gold electrode at −1.2 V (Fig. 1b) is compared with the UV Raman spectrum of 0.01 M aqueous thymine and 0.1 M KCl (Fig. 1a). The bands at 1022 and 1486 cm^{-1} are hardly observed in Fig. 1a; however, the two modes can be observed from the Au electrode at the given potentials. From the solution, the ring stretch mode appeared at 1238 cm^{-1} is much greater than the CH_3-rocking mode at 1174 cm^{-1}; from the gold electrode surface, however, the similar mode at 1238 cm^{-1}is weaker than the 1174 cm^{-1} peak at the given potential. The same phenomenon occurs at 1597 and 1670 cm^{-1}, which are both assigned to the in-plane C=O strech mode. Very interestingly, the bands at 622, 749 and 809 cm^{-1} in the thymine solution Raman spectrum exhibited a blueshift in the surface Raman spectrum of thymine on the Au electrode. The blueshift of these bands may indicate a weak interaction of the aromatic rings on the gold surfaces.

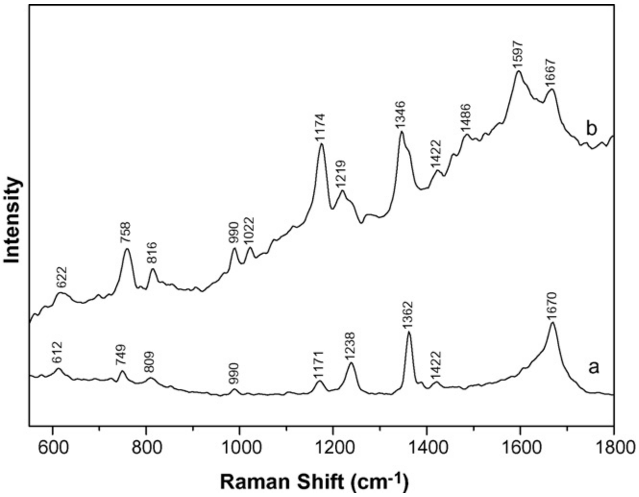

Fig. 1. (a) The UV Raman spectrum of 0.01 M aqueous thymine and 0.1 M KCl. (b) Surface Raman spectrum of Thymine adsorbed on a gold electrode from abulk solution of 0.01 M thymine and 0.1 KCl. Electrode potential = −1.2 V. Excitation line = 325 nm.

Fig. 2 shows the potential-dependent surface spectra of thymine adsorbed on the roughened Au electrode with ultraviolet 325 nm excitation. The solution was 0.01 M thymine and 0.1 M KCl. It can be observed that with a negative potential shift

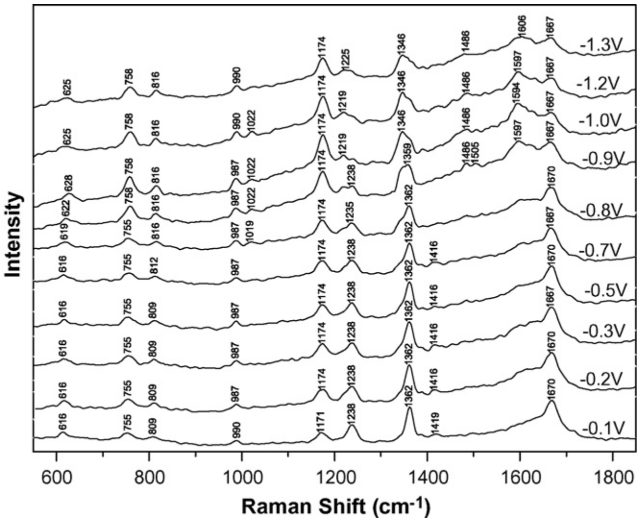

Fig. 2. The potential-dependent surface spectra of thymine adsorbed on the Au electrode with ultraviolet 325 nm excitation. The solution was 0.01 M thymine and 0.1 M KCl.