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The reorientation of benzonitrile on Platinum electrode probed by surface enhanced Raman spectroscopy

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ABSTRACT

The adsorption and reorientation behavior of benzonitrile on an electrochemical roughened Pt electrode were studied by surface-enhanced Raman spectroscopy (SERS) over a wide potential range. The results revealed that benzonitrile was adsorbed on the surface in a vertical orientation through the nitrogen atom of CN group in the relative positive potential region (>-0.6 V), while the benzonitrile molecule changed its orientation with the negative movement of potential (<-0.8 V). In the hydrogen evolution region, the intensity of the Raman bands from the benzene ring and CN group decreased dramatically, and the frequency of CN red-shifted about 160 cm^{-1}. It indicated that the benzonitrile was adsorbed on the Pt electrode in a flat orientation by interacting with the electrode surface via CN and/or benzene ring. A schematic model about the adsorption configurations of benzonitrile in different potential regions was proposed.

1. Introduction

The orientation and bonding of surface adsorbate is one of the fundamental issues in surface electrochemistry. Such information can be obtained from vibrational spectroscopy by utilizing so-called surface selection rules to analyse the intensities of vibrational bands [1–5]. Therefore, various vibrational spectroscopic techniques have been applied to the studies of adsorbed molecules [6–12], particularly for aromatic molecules that were considered models for studying the adsorption and reaction on metal surfaces. These techniques include electron energy loss spectroscopy (EELS), sum frequency generation (SFG), infrared and Raman spectroscopy. In particular, surface-enhanced Raman spectroscopy (SERS) has been shown to be a powerful technique for determining the orientation of molecules adsorbed on electrode surfaces [9,11–16]. Most importantly, SERS can yield detailed vibrational information free from the interference of the bulk-phase even at the metal-liquid interfaces and can work without the vacuum condition. However, this enhancement effect has been mainly restricted to the noble metals Ag, Au and Cu for a long period after the discovery of SERS [13–18]. In the past decade, by utilizing different types of surface roughening procedures and employing the high sensitivity of confocal Raman system, high quality spectra of some organic molecules and inorganic ions on transition metals such as Pt, Ni, Pd, Ru, Rh, Fe, Co, Zn have been obtained successfully in our group [19–21]. It has been shown that the electrochemical pretreatments play an important role for obtaining the surface Raman spectra from pure transition-metal surfaces [19]. As a consequence of these efforts, it has been possible to study the adsorption and reaction of various molecules, including pyridine, pyrizine, benzene and cyanide, on pure transition metals by SERS [19]. Here, benzonitrile was used as a model molecule for studying the surface bonding and adsorption reorientation on the Pt surface in view of its special molecular structure with benzene ring and C$\equiv$N group [22]. For the former, it can be served as an electron donor or acceptor due to the electron source of the π bond. Moreover, our previous studies on the adsorption of benzene indicated that the frequency of the stretching vibrational mode has a remarkable red-shift because of the interaction of the π electrons of the benzene ring with the metal surface [5,23]. Thus, the change of the frequency in the Raman spectra can provide information for determining the adsorption orientation. Most importantly, the characteristic C$\equiv$N stretching vibrational mode of benzonitrile shows very strong signal and sharp band shape in the Raman spectrum, and it is located in the relative high wavenumber region (2000–2300 cm^{-1}), where the interference of solvent signal and the coupling of other bands of the molecule itself can be negligible. Furthermore, our previous studies of CN^- adsorbed on Pt revealed that the frequency of C$\equiv$N exhibited a large shift with the applied electrode potential due to the strong electrochemical Stark effect [24]. Therefore, by correlating the SERS of the benzene ring and

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the C≡N group of benzonitrile adsorbed on Pt electrodes we may be able to extract rich information for deducing the orientation of the molecule on the surface [22]. On the basis of the above structural characteristic, benzonitrile is chosen as a model adsorbate for investigation of the adsorbate-metal interaction. So far, several spectroelectrochemical studies on the adsorption of benzonitrile at electrode surfaces have been reported. Nakayama et al. studied the adsorption states of benzonitrile and alkyl cyanides on evaporated nickel and palladium films by X-ray photoelectron spectroscopy [25]. They found that benzonitrile is adsorbed on the surface with rehybridization of CN triple bond rather than the π interaction through the aromatic ring. Lipkowski et al. quantitatively studied the adsorption of benzonitriles on Au(111) by chronocoulometry [26–28]. The Gibbs energy of adsorption was determined and adsorbed benzonitrile molecules were oriented parallel to the electrode surface at negative and moderately positive potentials and low bulk concentrations. The FT-IR studies showed that benzonitrile molecules were totally desorbed from the Au(111) surface at potentials more negative than −0.6 V (SCE) and they were adsorbed at the gold surface at more positive potentials with a dissociative character. Therefore, some thermodynamic and infrared spectral evidence suggested that benzonitrile was bound "flat" on Au(111) electrodes at more negative potentials. A similar orientation has been deduced from EELS for benzonitrile on Cu(111) and on Au(100) in UHV [29,30]. Recently, Xu et al. reported the covalent attachment and binding configuration of benzonitrile on Si(100) deduced from temperature-programmed desorption (TPD), high-resolution electron energy loss spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and DFT calculations [22,31]. They proposed 10 adsorption configurations based on the experimental and simulation.

However, most of these studies were restricted to the UHV environment or on the single crystal metal surfaces. It is well known that the adsorption of a same species in the UHV system could be very different from that in the electrochemical system, because the adsorption process in the latter system may be influenced by the applied potential, the solvent and surface structure. The metal-dependent nature of surface–chemisorbate interactions has also been systematically investigated by Weaver and his coworkers in electrochemical systems for surfaces including Au electrodes and Pt, Pd, Rh, Ir ultrathin film coated Au electrodes [32–38]. Actually, the first SERS study of benzonitrile adsorbed on Au was reported by Gao and Weaver [36]. They proposed a vertical orientation of benzonitrile at more positive potentials. However, SERS study of benzonitrile on silver sols and electrodes reveal either "end-on" or "face-on" orientations [39,40], with the nitrile group nonetheless providing the primary surface anchor. With the aid of the long-range effect of the electromagnetic (EM) enhancement created by the SERS-active substrate underneath, SERS spectra of benzonitrile on ultrathin films of platinum group metals have been obtained. The SERS spectra were compared with DFT studies, which was based on the binding of the nitrile group to metal atoms and small metal clusters, and thus the benzonitrile surface coordination was modeled [37]. They found that the metal-dependent SERS $\nu_{C\equiv N}$ behavior exhibited the $\nu_{C\equiv N}$ redshift in the sequence $Cu < Ag < Au \approx Pt < Pd \sim Rh \sim Ir$. Their findings provided a clear illustration of the utility of the "overlayer SERS" strategy for exploring metal-dependent bonding of complex organic adsorbates in electrochemical environments.

In this paper, we reported a study of potential-dependent surface Raman spectra and reorientation of benzonitrile adsorbed on electrochemical roughened pure Pt electrodes in order to understand how the applied potentials influence the interaction of benzonitrile.

2. Experimental

Raman spectroscopic measurements were performed on a confocal microprobe Raman system (LabRam I, Dilor). A holographic notch filter and a CCD detector were equipped, and thus it has a very high sensitivity. The microscope attachment was based on an Olympus BX40 system and used a 50 × long working length objective (about 8 mm) so that the objective will not be immersed in the electrolyte. The sizes of the slit and pinhole in the present study were set at 200 and 400 μm, respectively. The diameter of the laser spot on the electrode is ca. 3 μm. All the experiments were done using the excitation line of 632.8 nm from an internal He–Ne laser with a power of 12 mW on the electrode surface.

The working electrodes were polycrystalline Pt disk with a geometric area of 0.1 cm^2 embedded in a teflon shroud. A detailed description of the roughening procedure of Pt electrode for producing SERS activity could be obtained from Ref. [29]. Prior to the electrochemical SERS measurements, the roughened electrode was cycled in the 0.5 M H_2SO_4 solution in the potential range from −0.3 V to 1.2 V for several minutes to remove metastable surface clusters and obtain a stable surface. After the electrochemical pretreatments, the electrode was rinsed thoroughly with Milli-Q water and transferred to the spectroelectrochemical cell for further measurements. The electrode potential during the Raman measurements was controlled by a PAR 173 potentiostat (EG&G). A large Pt ring served as the counter electrode. The reference electrode was a saturated calomel electrode (SCE), thus all the potential quoted here are with respect to SCE. The detailed description of the spectroelectrochemical measurement has been given elsewhere [24]. All experiments were performed at room temperature. All the chemicals used were analytical reagent and the solutions were prepared using Milli-Q water.

3. Results and discussion

Curve a and b in Fig. 1 are the cyclic voltammograms of a roughened Pt electrode in 0.1 M $NaClO_4$ and in 20 mM C_6H_5CN + 0.1 M $NaClO_4$ solutions, respectively. We can find that the characteristic hydrogen related processes that exist in the pure $NaClO_4$ solution are completely blocked in the solution containing benzonitrile. It reveals that the benzonitrile can be strongly adsorbed on the Pt

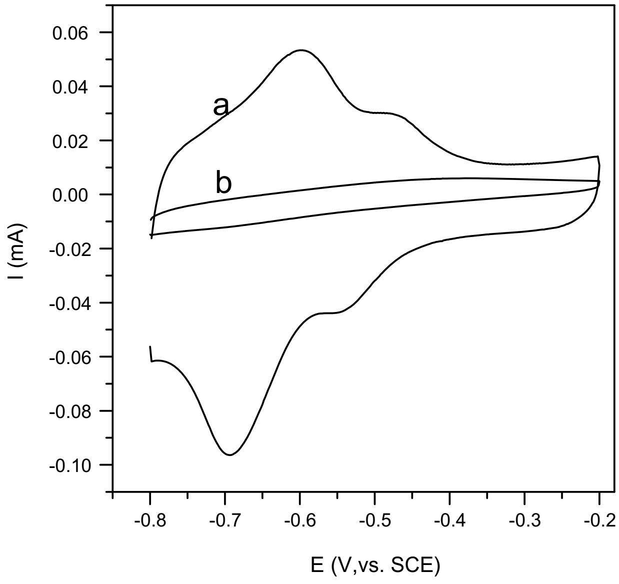

Fig. 1. Cyclic voltammograms of a roughened Pt electrode in solutions of 0.1 mol/dm^3 $NaClO_4$ (a) and 20 mM C_6H_5CN + 0.1 M $NaClO_4$ and (b) scan rate: 100 mV s^{-1}.