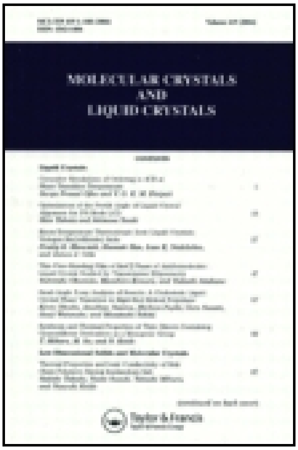

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Irreversible Adsorption and Reduction of *p*-Nitrothio-Phenol Monolayers on Gold: Electrochemical *in Situ* Surface Enhanced Raman Spectroscopy*

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The redox behavior of *p*-nitrothiophenol (*p*-NTP) monolayers on gold was studied by electrochemical *in situ* surface enhanced Raman spectroscopy (SERS). The chemical adsorption of *p*-NTP on gold through Au-S bonding was confirmed by the comparison between the Raman spectra of parent molecules and that of the monolayer. The irreversible reduction of *p*-NTP monolayers to *p*-aminothiophenol (*p*-ATP) monolayers was evidenced by the observed potential dependent spectral changes. The present results demonstrated the potential of SERS in investigating the adsorbate-substrate interaction and in monitoring surface reactions at a monolayer scale.

Keywords: Thiophenols; Monolayers; SERS; *in situ*

INTRODUCTION

Surface enhanced Raman spectroscopy (SERS) has been developed as a powerful and sensitive tool for surface analysis. Recently, efforts have been made in both developing its technique and investigating its mechanism. For example, SERS has been used to provide molecular conformational information of *n*-alkanethiols self-assembled monolayers (SAMs)[1,2], and to follow photochemical or electrochemical reactions in monolayer systems[3-5].

An electrochemical *in-situ* micro-Raman measurement setup was built in our group and has been used successfully in confirming the redox process between azobenzene and hydrazobenzene in SAMs on gold[6]. Recently, our investigations of SERS have been extended to 2-dimensional Raman mapping[7], novel SERS-active system constructing[8], as well as Raman titration technique developing[9]. In this work, a fundamental study of the

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interaction of *p*-NTP molecules with gold substrate and the redox properties of thus formed monolayers will be reported.

EXPERIMENTAL

The electrochemical *in situ* Raman system was constructed by combining a Renishaw System 1000 Ramanscope Spectrometer (Renishaw plc, UK) with an electrochemical measurement system (Hokuto Denko, Japan)[6]. The spectroelectrochemical cell is specially designed to fit the sample stage of the microscope below the 50×objective. The working electrode is a 1.0 mm diameter gold disk sheathed in Teflon, which has been skid polished and pretreated by oxidation-reduction cycling method to give a SERS-active surface. An Ag/AgCl (sat. KCl) and a Pt wire were used as reference electrode and counter electrode, respectively.

p-Nitrothiophenol (*p*-NTP) was from Aldrich. Ultrapure water with a resistance >16.5 MΩ·cm was used throughout the experiments. The monolayers of *p*-NTP were prepared by adsorption of parent molecules from the dilute ethanolic solutions onto the gold electrodes. To get rid of the possible physisorbed *p*-NTP from the electrode surface, the electrode was carefully rinsed with ethanol and water.

RESULTS AND DISCUSSION

p-NTP monolayers are both photoactive and electroactive, they were considered as model systems for photoelectrochemical information storage[10], and for the study of the reduction mechanism of nitro-substituted aromatics. Fig. 1 shows typical SERS spectra of *p*-NTP monolayers on gold (dashed line) and normal Raman spectra of *p*-NTP powder (solid line). Major bands of *p*-NTP[5], *e.g.*, 1576 cm^{-1} for ν(C-C)+β(C-H), 1336 cm^{-1} for ν_{sym} (NO_2), and the doublet at 1080-1110 cm^{-1} for β(CCC)+ν(C-S), 850 cm^{-1} for π(C-H)[11], can be clearly identified in the SERS spectra, only with slight differences in peak position and relative intensity from the spectrum of the powder (Fig. 1a). The similarity between these spectra hinds the factor that *p*-NTP monolayers have rather low surface coverage without strong lateral interactions. However, the band for ν(S-H) around 2550 cm^{-1} did not appear in the SERS spectrum (Fig. 1b), indicating that the thiophenols were anchored to gold through Au-S bonding. Futamata has shown that *p*-NTP chemisorbed onto silver via Ag-S bonding[5], the much higher S/N shown in Fig. 1b give us more confidence in drawing such a conclusion for the *p*-NTP adsorption on gold.

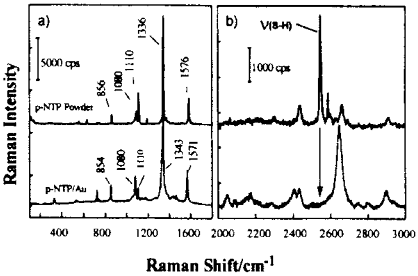
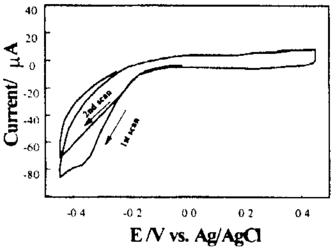


FIGURE 1 SERS of *p*-NTP SAM on gold (dashed line) and normal spectra of *p*-NTP powder(solid line). a) 150 to 1800 cm^{-1} ; b) 2000 to 3000 cm^{-1}.

Fig. 2 presents the cyclic voltammograms (CVs) of *p*-NTP monolayers on gold electrode within a sweeping range from -0.45V to +0.45V. For the cathodic scan (0.0V → -0.45V) in the first cycle, a reduction wave appeared around -0.35V (*vs*. Ag/AgCl), but no oxidation peak was observed for the successive anodic scan (-0.45 → 0.0V → 0.45V). For the second cycle, the reduction current decreased to a large extent. After several scans, neither reduction nor oxidation peak can be obtained.



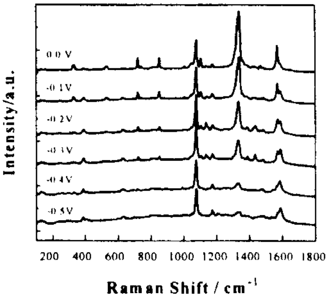


FIGURE 2(*left*) Cyclic voltammograms of *p*-NTP monolayers on gold in the scan range of -0.45V ~ +0.45V.

FIGURE 3(*right*) Potential dependent SERS spectra of *p*-NTP SAMs on Au. Excitation: 632.8 nm; Power: 0.5 mW; Exposure: 8.5s.

The potential dependent SERS spectra (Fig. 3) from *p*-NTP monolayer on gold were successfully recorded in order to follow its redox behavior. Firstly, the intensity of the band at 1343 cm^{-1} decreases when the applied electrode potential goes to negative, with a distinct change occurring between -0.3V and -0.4V, where the reduction wave has been observed in the CV (Fig. 2). Since this band has been assigned to the $\nu_{sym}(NO_2)$, the decrease in the band intensity should relate to the diminution of $-NO_2$ species resulting from the electrochemical reduction of $-NO_2$ groups. Secondly, the relative intensity of two bands around 1570 to 1590 cm^{-1} changed drastically, with one (1571cm^{-1}) dominated at 0.0V and disappeared at -0.5V, while the other (1592 cm^{-1}) initially appeared at 0.0V but dominated at -0.5V. Since these two bands are known as the characteristic stretch modes of the benzene ring substituted with $-NO_2$ (1571 cm^{-1}) and $-NH_2$ (1592 cm^{-1}), respectively. Such a relative intensity change is no doubt an indication for the reduction of *p*-NTP to *p*-ATP during the potential sweeping. In addition, SERS features related to *p*-NTP can not be recovered even though the electrode potential was stepped back to the positive side, suggesting that the above transformation is an irreversible process.

Based on above observations, the electrochemical reduction of *p*-NTP monolayers on gold can be considered as that the *p*-NTP monolayer is fully irreversibly reduced to *p*-ATP monolayer. This irreversible response is well account for the irreversible voltammetric response shown in Fig. 2. It also resembles the results reported for the *p*-NTP monolayers on silver, which has been correlated with the irreversible reduction of the nitro groups to the amino groups[5].

In summary, the formation of *p*-NTP monolayers on gold based on Au-S bonding and the irreversible reduction of *p*-NTP monolayers to *p*-ATP monolayers have been successfully addressed by our electrochemical *in situ* SERS investigations. This work clearly shows the potential of SERS as a sensitive tool to elucidate the interaction between adsorbates and substrates and to describe the reaction diagram on surface at the monolayer scale.

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[11] ν, β, and π stand for *stretching*, *in-plane-bending*, and *wagging* modes, respectively.