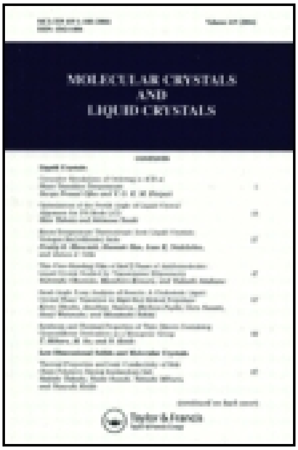

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ELECTROCHEMICAL IN-SITU RAMAN STUDY OF AZOBENZENE SELF-ASSEMBLED MONOLAYERS ON GOLD

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Abstract An electrochemical in-situ micro-Raman spectroscopy system has been built and used to follow the reduction/oxidation of functional groups within self-assembled monolayers (SAMs) on gold. For the first time, the different electrochemical accessibility of two typical azobenzene SAMs has been successfully addressed by using this system.

INTRODUCTION

By molecular design, we have succeeded in the creation and characterization of a series of novel azobenzene self-assembled monolayers (SAMs) with varied terminal groups and alkyl spacers[1,2]. The electrochemical properties of these azobenzene monolayers have been extensively studied, which show very different voltammetric behaviors. For instance, some of these monolayers show clear-cut faradic responses in aqueous medium, while others not. We noted that the electrochemically inactive azobenzene SAMs always have long terminal alkyl groups, which are believed to contribute to the more closely-packed monolayer structures[2]. Although the closely packed and highly oriented monolayer structure might interfere with the conformational change and protonation involved in the complex reaction of azobenzene groups, detailed data to correlate electrochemical behaviors of different azobenzene SAMs with their molecular and monolayer structures are still insufficient due to the difficulties in conventional spectroscopic measurement of monolayer in aqueous solution. We have been trying to construct a novel electrochemical in-situ surface enhanced Raman scattering (SERS) measurement system[3]. In this work, two typical azobenzene SAMs were chosen as the model systems to demonstrate the usefulness of this in-situ technique in investigating the reduction/oxidation of azobenzene SAMs.

EXPERIMENTAL

The molecular structures of the two typical azobenzene derivatives used in the present study were shown in Scheme I.

Scheme I

C0AzoC2SH C8AzoC3SH

The electrochemical in-situ SERS system used in the present work was constructed by combining a Renishaw System 1000 Ramascope Spectrometer with an electrochemical measurement system. The spectroelectrochemical cell is specially designed, which can be mounted on the sample stage of the microscope just below the 50× objective. The working electrode is a 1.0mm 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. The azobenzene self-assembled monolayers were prepared by chemisorption of C0AzoC2SH and C8AzoC3SH molecules from their ethanolic solutions onto the gold electrodes.

RESULTS AND DISCUSSION

Both C0AzoC2SH and C8AzoC3SH spontaneously adsorb onto gold surface and form stable and well organized monolayers, which have been evidenced by the contact angle measurements and electrochemical characterizations. Figure 1 shows the cyclic voltammograms of C0AzoC2SH and C8AzoC3SH SAMs on gold electrodes. The SAM of C0AzoC2SH exhibited a well-behaved electrochemical response with a very large anodic-cathodic peak separation (Figure 1a), similar to that we have observed previously for the C2AzoC2SH SAM[1]. The electrochemical response has been attributed to the $2e^-$, $2H^+$ reduction/oxidation of the azobenzene group. However, for the SAM of C8AzoC3SH, no discernible redox peaks were observed in its cyclic voltammogram (see Figure 1b), suggesting that the azobenzene groups within C8AzoC3SH SAM did not undergo electrochemical reduction/oxidation at least in the experimental conditions.

The in-situ potential dependent SERS spectra acquired from the two azobenzene SAMs were given in Figure 2. The electrode potential was controlled in a way as labeled at the right side of each figure. In these spectra, the multiple bands in the 1100-1650cm^{-1} region, assigned to ϕ-N stretching ($\nu_{\phi\text{-}N=}$), N=N stretching ($\nu_{N=N}$) and benzene ring vibrations, are characteristics of the azobenzene moiety[4]. As shown in Figure 2a, for C0AzoC2SH SAM, on the potential going negative direction (-0.15V → -0.45V), Raman bands for $\nu_{\phi\text{-}N}$=(1143, 1185cm^{-1}), $\nu_{N=N}$ (1445cm^{-1}) and benzene ring (1406cm^{-1})

gradually decreased and finally vanished, suggesting that the azobenzene group was reduced to its hydrazobenzene form. For hydrazobenzene, only the band at $1603cm^{-1}$ for quadrant-stretching of the ***para***-disubstituted benzene ring can be seen, while others from N-related groups are too weak to be discernible[4]. Another remarkable feature in these spectra is that by oxidation (potential going positive direction, i.e., -0.45V→-0.15V→+0.15V), all of the Raman bands mentioned above recovered to their original patterns excellently, indicating that the hydrazobenzene was re-oxidized to the azobenzene form. These observations confirmed that azobenzene molecules in the monolayer do undergo a reversible reduction/oxidation between azobenzene and hydrazobenzene during the potential sweeping.

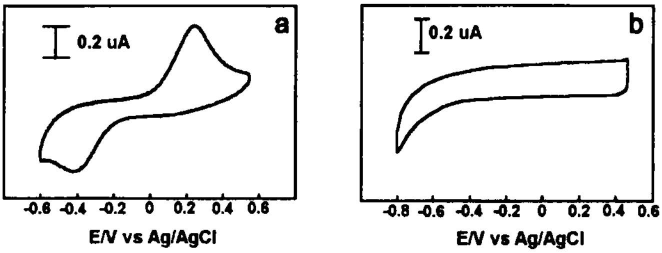

FIGURE 1 Cyclic voltammograms of a) C0AzoC2/Au and b) C8AzoC3/Au SAMs in Britton-Robinson buffer, pH 5.0, 0.1 mol·dm^{-3} $NaClO_4$. Scan rate: 0.05V/s.

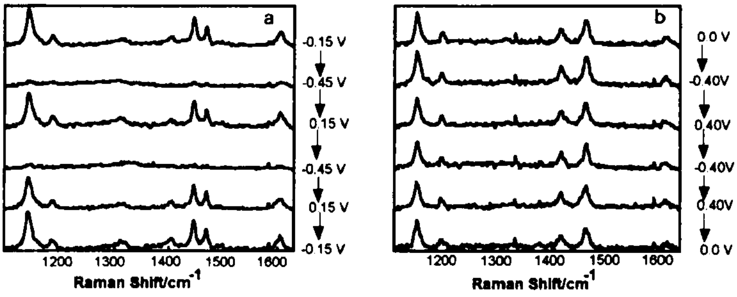

FIGURE 2 Potential dependent SERS spectra for a) C0AzoC2/Au and b) C8AzoC3/Au SAMs. Exposure: 632.8nm, 5mW, 30s

The appearance of Raman spectrum from C8AzoC3SH SAM (see Figure 2b) is very similar to that of C0AzoC2SH SAM (Figure 2a). This is reasonable because the spectral feature in the examined region is dominated by the azobenzene chromophore rather than other groups in the molecular structure. Comparing the sequential Raman spectra of C8AzoC3SH SAM obtained at different potentials, no discernible change in either frequencies or intensities for $\nu_{\phi\text{-}N=}$ (1141, $1188cm^{-1}$), $\nu_{N=N}$ ($1457cm^{-1}$) and bands of benzene ring vibration(1412, 1603cm^{-1}) was observed within a even larger potential window and a longer collection time. The absence of the potential-dependent spectral change enables us to conclude that the reduction of the azobenzene to hydrazobenzene can not be carried out in this monolayer.

Since the reduction/oxidation of azobenzene group involves two structure-dependent processes, i.e., the molecular conformational change and the incorporation of protons, the different electrochemical accessibility of azobenzene groups in C0AzoC2SH and C8AzoC3SH SAMs might be attributed to the different monolayer structures. The discussion about the electrochemical accessibility of SAMs has been preliminarily touched by Mirkin et al[5]. They found that in a ferrocenyl terminated azobenzene SAM on gold, the outer ferrocenyl layer is electrochemically accessible while the interior azobenzene layer is not. They proposed that the inhibition of ion transportation into the azobenzene layer by the tightly-packed monolayer is responsible for the electrochemical inaccessibility of the azobenzene groups.

The magnitude of contact angle can be used as an indicator for the surface hydrophobicity, which is determined by both the nature of surface groups and the packing density of the monolayer. The different advancing contact angles with water for C8AzoC3SH SAM (109°) and C0AzoC2SH SAM (85°) indicate that C8AzoC3SH SAM might have a more hydrophobic surface and probably a more closely-packed monolayer structure than the latter. In our previous study, we have found that the packing density of SAMs derived from CnAzoC2 increased with the carbon number in the terminal alkyl chain (n=1,2,3,4)[2]. Since C8AzoC3SH has a long alkyl end group, a more densely-packed structure is expected for its SAM than that of C0AzoC2SH due to the strong hydrophobic interactions between the terminal alkyl chains. Taking together, the less densely-packed and less hydrophobic C0AzoC2SH SAM can provide free space both for the structural change of the azobenzene group and for the transport of protons from solution side to redox center, thus allowing the 2e$^-$, 2H$^+$ reduction/oxidation of the azobenzene chromophore. On the contrary, in the case of the C8AzoC3SH SAM, both structural conformational change and transportation of protons to the active center are prohibited. As a consequence, the SAM exhibited electrochemically inactive behavior.

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