Simple azo derivatization on 4-aminothiophenol/Au monolayer

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Abstract

A stable and redox active monolayer of para-mercaptodiazoaminobenzene was achieved by direct diazotization on 4-aminothiophenol/Au monolayer. Electrochemical and surface-enhanced Raman scattering spectroscopy measurements were conducted before and after the reaction. The CV result, which exhibits two steps of reversible one-electron and one-proton oxidation and reduction, confirmed the grafting structure on 4-ATP monolayer.

Keywords: p-Mercaptodiazoaminobenzene; Self-assembled monolayers; SERS

1. Introduction

Self-assembling technique, as a promising method of interfacial modification in the molecular scale, has received great interest within past decade. It has been examined widely from both fundamental and applied perspectives [1]. Recently, azobenzene-based alkanethiol self-assembled monolayers (SAMs) have attracted much interest, since azobenzene-based molecules have been proven to be a potential medium for high-density recording elements, molecular switches, etc [2–8]. SAMs of the azobenzene have been used to investigate the generation and mechanism of SERS [8–13] due to the large Raman scattering cross section of azobenzene group [3,4,14]. And the electrochemistry of such azobenzene SAMs have also been studied extensively [8,11,12,15]. Diazoaminobenzene (DAAB), an analogue of azobenzene, is also of a great interest. DAAB has been identified as an impurity in a number of dyes and coloring agents that are components of cosmetics, food products, and pharmaceuticals and was selected for metabolism and toxicity studies by the National Toxicology Program (NTP) in the United States based on the potential for human exposure, positive Salmonella data, and lack of adequate toxicological data [16]. Meanwhile, it shows semiconducting properties and a phenomenon of phase transition [17] and can chelate transition metals into metal complexes which show electrical and magnetic performances [18]. However, till recently, very little attention has been paid to it because of its difficult preparation and purification originated from its thermal instability.

Herein, a simple azo derivatization directly on 4-ATP/Au monolayer was reported. Upon diazotization, aniline is covalently grafted on the 4-ATP monolayer, thus a stable and redox active para-mercaptodiazoaminobenzene monolayer was obtained. The resultant monolayer was confirmed by electrochemistry and surface-enhanced Raman scattering spectroscopy (SERS).
2. Experimental procedure

2.1. Preparation of the modified electrode

Prior to the modification of 4-ATP monolayer, the working Au electrode should be cleaned and roughened. At first, it was polished successively with 1.0 and 0.3 μm of alumina slurry to a mirror-like substrate, and was rinsed copiously with water, and then was scanned in 1 M H₂SO₄ solution until a stable voltammogram corresponding to a clean, unmodified gold electrode surface was obtained. After that, the cleaned Au electrode was roughened in a separate cell using a traditional oxidation–reduction cycling (ORC) similar to previous report by Liu [19] and was immersed immediately in ethanol solution of 1 mM 4-ATP for 10 h. After this immersion, the roughened Au substrate modified with a 4-ATP monolayer was cleaned completely with ethanol and water to remove unreacted thiol component and dried.

2.2. Reaction of diazotization and coupling

After that, the 4-ATP-modified Au electrode was transferred into 0.1 M HCl solution at 2–4 °C, and 100 mg NaNO₂ was added slowly, the total concentration is about 0.05 M, which is a little excess to ensure the completeness of the reaction. After 30 min incubation, the Au electrode was removed and rinsed with icy water immediately. Then, it immersed into 0.025 M aniline solution (pH 5). This reaction lasted for 30 min and was stirred slightly. Finally, the Au electrode was removed from the solution and rinsed with Ultrapure water (18 MΩ, Millipore) thoroughly and dried (whole procedures were illustrated in Scheme 1).

2.3. Equipments

Electrochemical measurements were conducted with CHI660A Electrochemical workstation (CHI, USA) using a conventional three-electrode one-compartment cell with a polycrystalline Au working electrode (3 mm diameter), a spiral Pt wire counter electrode, and Ag/AgCl reference electrode (in a saturated KCl solution). Raman spectra were obtained using a JY-T64000 Raman Scattering Spectrometer (Jobin–Yvon, France) equipped with a Ti:Sapphire CW Tunable Laser (model 3900 S, and 798.447 nm excitation in our use) and a multichannel CCD detector cooling with liquid nitrogen (to 139 K).

3. Results and discussion

3.1. SERS measurements of this derivatization

SERS was used to investigate the presence and structure of 4-ATP monolayer on a roughened Au surface and a SERS spectrum with a high S/N ratio was obtained. The SERS spectrum of 4-ATP on the roughened Au substrate is shown in Fig. 1 (curve a). Our result is great consistent with previous report of M. Osawa et al. [21].

As can be seen from Fig. 1 (curve a), a strongest band can be observed at ca. 1081 cm⁻¹ which is assigned to C(benzene ring)–S stretching vibration, while the relational band located at 1590 cm⁻¹ is assigned to C–C stretching vibration of benzene rings. The band at 1007 cm⁻¹ is originated from C–C bending vibration. Importantly, the bands located at 1141 and 1427 cm⁻¹ ascribed to the charge transfer of the metal to the adsorbed molecules can also be seen clearly, where it suggests a perpendicular orientation of 4-ATP unit to the metal surface [20–22].

The difference of the SERS spectra after diazotization is shown in curve b in Fig. 1. A new peak located at about 1340 cm⁻¹, which is assigned to N≡N stretch-
ing vibration, is the major difference. Our result is very similar to those previous reports [11,13], in which the band located at about 1410 cm$^{-1}$ is attributed to N=N stretching vibration. The vibration frequency shift of N=N stretching in our work may be originated from the high molecular resonance of the whole system due to the conjugated bridge via 4-ATP. More detail assignments of those Raman bands are listed in Table 1.

3.2. Electrochemical responses of the azo-derivatized monolayer

The diazotization-coupling reaction was confirmed further by electrochemical measurement. The results are shown in Figs. 2 and 3, after the derivatization, characteristic CV peaks of azo groups can be found clearly.

Fig. 2 shows an obvious difference from these CV curves before (a) and after (b) diazotization reaction. The upper curve (a) is the result of 4-ATP/Au in 0.1 M NaClO$_4$ in B–R buffer (pH 5.0) in the first sweep, which reveals the formation of a kind of radical cation of 4-ATP monolayer [23]. The bottom one (b) is the result after the diazotization-coupling reaction, which is quite similar to the recent report in AzoC$_2$SH/Au SAMs [15], where they were treated as a cis-isomer of para-mercaptodiazoaminobenzene. The CV curve exhibits two steps of reversible one-electron and one-proton oxidation and reduction well.

The azo-derivatized SAM electrode shows a typical quasi-reversible cyclic voltammogram with a small, although not zero $\Delta E_p$ (ca. 30–33 mV at our studied scan rates, here lower than 1.2 V/s), which is assigned to the redox reaction of the azo moiety on the surface, as shown in Figs. 2 and 3. The current of these anodic and cathodic peaks is directly proportional to the scan rate from a quite lower to 1200 mV even higher (a plot of the anodic current at lower potential against scan rates is exemplified in Fig. 3), confirming a surface reaction of these derivatized azo moieties.

Table 1
Vibration modes observed by SERS spectroscopy on 4-ATP-modified Au

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Assignments</th>
</tr>
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<tbody>
<tr>
<td>1590</td>
<td>$\nu$(CC)</td>
</tr>
<tr>
<td>1489</td>
<td>$\nu$(CC) + $\delta$(CH)</td>
</tr>
<tr>
<td>1427</td>
<td>$\nu$(CC) + $\delta$(CH)</td>
</tr>
<tr>
<td>1386</td>
<td>$\delta$(CH) + $\nu$(CC)</td>
</tr>
<tr>
<td>1179</td>
<td>$\delta$(CH)</td>
</tr>
<tr>
<td>1141</td>
<td>$\gamma$(CCC) + $\gamma$(CC)</td>
</tr>
<tr>
<td>1081</td>
<td>$\pi$(CS)</td>
</tr>
<tr>
<td>1007</td>
<td>$\gamma$(CCC) + $\gamma$(CC)</td>
</tr>
<tr>
<td>816</td>
<td>$\pi$(CH)</td>
</tr>
<tr>
<td>705</td>
<td>$\pi$(CS) + $\pi$(CH) + $\pi$(CC)</td>
</tr>
<tr>
<td>639</td>
<td>$\gamma$(CCC)</td>
</tr>
</tbody>
</table>

Fig. 2. CV curves of: (a) 4-ATP/Au before the derivatization; (b) after the derivatization of 4-ATP SAM and aniline; conditions: 0.1 M NaClO$_4$ in B–R buffer (pH 5.0), scan rate 0.1 V/s.

Fig. 3. CV curves of para-mercaptodiazoaminobenzene monolayer on Au at different scan rates, from a to k corresponding to 100–1000, 1200 mV/s, respectively. Inset: plot of anodic peak current vs. scan rate.

The azo-derivatized SAM form a pendant structure on the 4-ATP monolayer. Then, the wider voltammetric shape should be originated from the intermolecular ste-
ric repulsion of those derivatized aminoazo moieties on 4-ATP SAM, as illustrated in Scheme 1.

The peak-to-peak potential difference almost keeps constant, at least in our studied range of scan rates. Such characteristic should be attributed mainly to the fact that the redox moiety, azo, is coupled with a conjugated underlayer, 4-ATP layer, where can undergo an excellent electron transfer.

The azo-derivatized monolayer also shows a great stability and reproducibility, almost no obvious desorption can be observed after multi-cycles potential running (data not shown here).

4. Conclusions

SERS spectrum of 4-ATP monolayer on roughened gold electrode with a high S/N ratio was obtained. And a stable and redox active para-mercaptodiazonobenzene monolayer has been fabricated on a 4-ATP SAM via a simple chemical derivatization. The highly resonant and electroactive monolayer may have potential uses in the future.

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References