

## Study on surface acid-base property of carboxylic acid-terminated self-assembled monolayers by cyclic voltammetry and electrochemical impedance spectroscopy

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Cyclic voltammetry and electrochemical impedance spectroscopy were used to study the surface acid-base property of carboxylic acid-terminated self-assembled monolayers (SAMs). A carboxylic acid-terminated thiol, such as thioctic acid (1,2-dithiolane-3-pentanoic acid), was self-assembled on gold electrodes. Electron transfer between the bulk solution and the SAM modified electrode was studied at different pH using  $\text{Fe}(\text{CN})_6^{3-}$  as a probe. The surface  $\text{p}K_a$  of thioctic acid was determined by cyclic voltammetry and electrochemical impedance spectroscopy to be  $5.6 \pm 0.1$  and  $5.8 \pm 0.1$ , respectively. The method is compared with other methods of monolayer  $\text{p}K_a$  measurement.

**Keywords** Surface  $\text{p}K_a$ , self-assembled monolayer, cyclic voltammetry, electrochemical impedance

### Introduction

Studies of self-assembled monolayers (SAMs) on solid substrates have been the subject of considerable interest in the last decade. In particular, thiol modified gold electrode has been paid more and more attention since Nuzzo and Allara<sup>1</sup> showed that SAMs of alkanethiolates on gold could be prepared by adsorption from solution.<sup>2-5</sup> In addition, SAMs prepared by the spontaneous chemisorption of thiolates on gold can be used to create surface of controlled composition if the adsorbed molecule is terminated with a functional group  $-\text{COOH}$  or  $-\text{NH}_2$ . Such charge-regulated monolayer is very use-

ful for the adsorption of protein,<sup>6</sup> polyelectrolyte,<sup>7</sup> and other species.<sup>8-10</sup>

Determination and control of surface  $\text{p}K_a$  are of significance in both practice and theory. A few techniques have been used to estimate surface  $\text{p}K_a$  values. For example, Ward and co-workers<sup>11</sup> used a quartz crystal microbalance to investigate the property of carboxylate-terminated long-chain thiols, Brain and Whitesides<sup>12</sup> used an approach based on contact angle titration to estimate surface  $\text{p}K_a$  of carboxylic acid-terminated *n*-alkanethiol monolayers. Several groups have studied monolayers confined to the water/air interface using atomic force microscopy,<sup>13</sup> *ex-situ* infrared spectroscopy,<sup>14</sup> and surface-enhanced Raman spectroscopy.<sup>15</sup> There have also been reports that relate surfacial potential,<sup>16</sup> indirect laser-induced temperature jumper,<sup>17</sup> and differential capacitance<sup>18</sup> to the pH property of surface-confined monolayers. Recently, Brajter-Toth<sup>19</sup> has estimated the surface  $\text{p}K_a$  of carboxylic acid-terminated SAM on gold electrode using cyclic voltammetry. More recently, Calvo<sup>20</sup> has reported electrochemical impedance spectroscopy study of  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  electron transfer as a function of electrolyte pH at cystamine and thioacetate modified gold electrode.

In the previous work, we have reported the determination of surface  $\text{p}K_a$  of SAM and provided a theoretical simulation equation to relate the current signal to the

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fractional extent of monolayer protonation.<sup>21</sup> In the present paper, we wish to report our recent study on the surface acid-base property of carboxylic acid-terminated self-assembled monolayers combined with cyclic voltammetry and electrochemical impedance spectroscopy. A carboxylic acid-terminated thiol, such as thioctic acid (1,2-dithiolane-3-pentanoic acid, TA), was self-assembled on gold electrode. Electron transfer between the bulk solution and the SAM modified electrode was studied at different pH using  $\text{Fe}(\text{CN})_6^{3-}$  as a probe by cyclic voltammetry and electrochemical impedance spectroscopy. The surface  $\text{p}K_a$  of thioctic acid was determined by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The surface  $\text{p}K_a$  obtained was higher than the solution  $\text{p}K_a$  (*ca.* 5), which was consistent with similar systems by different methods.

## Experimental

### Materials

TA was purchased from Aldrich.  $\text{K}_3\text{Fe}(\text{CN})_6$  and  $\text{K}_4\text{Fe}(\text{CN})_6$  were supplied by Beijing Chemicals. All other chemicals were of analytical reagent grade. All solutions were prepared using super-pure water with a Millipore system. Phosphate buffer solution (PBS, 0.2 mol/L) containing 0.01 mol/L  $\text{KH}_2\text{PO}_4$  + 0.01 mol/L  $\text{K}_2\text{HPO}_4$  + 0.2 mol/L KCl was used as the supporting electrolyte.

### Electrode preparation

The gold disk electrode was constructed by sealing a piece of annealed gold wire (99.99%) in a special kind of soft glass. It was first polished with emery paper (Buehler, 3  $\mu\text{m}$ ) followed by alumina (Buehler, 1.0, 0.3 and 0.05  $\mu\text{m}$ , successively). After being sonicated in absolute ethanol, and then in water, it was electrocycled between 1.5 and  $-0.3$  V (*vs.* Ag/AgCl, saturated KCl) in 0.5 mol/L  $\text{H}_2\text{SO}_4$  until a reproducible voltammogram was obtained. The cleaned gold substrate was rinsed with super-pure water, and then immersed in 0.1% TA/ethanol solution for at least 24 h at room temperature to complete the formation of a monolayer. When removed from the solution, the SAM modified electrode was rinsed with copious amounts of absolute ethanol and super-pure water, respectively. Finally, it was trans-

ported into a cell for electrochemical measurements.

### Electrochemical measurements

The electrochemical measurements were performed in a single compartment cell at room temperature ( $20 \pm 2^\circ\text{C}$ ). A three-electrode setup was employed with an Ag/AgCl (saturated KCl) electrode as reference, a Pt wire as counter, and an SAM modified gold electrode as the working electrode. The cyclic voltammetric measurements were performed with a CHI 610 (CH Instruments, Inc. USA), controlled by IBM computer. The electrochemical impedance measurement was carried out using a Solartron potentiostat (Model 1286) connected to a Solartron frequency response analyzer (Model 1250). Before electrochemical measurements, the analytical electrolytes were purged with nitrogen for at least 15 min.

## Results and discussion

### Selection of supporting electrolytes

Phosphate buffer solution (PBS, 0.2 mol/L) containing 0.01 mol/L  $\text{KH}_2\text{PO}_4$  + 0.01 mol/L  $\text{K}_2\text{HPO}_4$  + 0.2 mol/L KCl was used as the supporting electrolyte throughout the experiments. This is based on the following two ideas: (1). Usually, the electrostatic binding interaction of terminal  $\text{NH}_3^+$  and  $\text{COO}^-$  groups of SAM and oppositely charged molecules is dependent on the solution pH and the ionic strength. Therefore, control of the solution pH and the ionic strength is of great importance. (2). In Brajter-Toth's<sup>19</sup> work, a strong acid-base titration has been applied to control the solution pH. However, the solution pH is hard to monitor accurately in the transition region. So a series of PBS is employed directly in our experiments to control the solution pH more conveniently.

### CV of $\text{Fe}(\text{CN})_6^{3-}$ at the bare gold electrode and the SAM modified gold electrode in different pH solution

Initially, the CV of 0.5 mmol/L  $\text{Fe}(\text{CN})_6^{3-}$  was recorded at bare gold electrode. The potential window used was from +0.6 to 0.0 V at scan rate 0.1 V/s. As expected, the CV response of  $\text{Fe}(\text{CN})_6^{3-}$  at bare gold electrode is independent of pH in PBS. Both peak current and peak potential remained essentially in the pH

range of 2–9. Therefore, CV of  $\text{Fe}(\text{CN})_6^{3-}$  at bare gold electrode is not affected by solution pH (data not shown here).

CV of  $\text{Fe}(\text{CN})_6^{3-}$  at the TA SAM modified gold electrode was also investigated in PBS of different pH. It should be noted that the potential window must be cautiously selected. For TA SAM modified gold electrode, the potential window selected here was from 0.7 to  $-0.2$  V,<sup>22</sup> where the electrode response and the background current do not change. On the contrary, the SAM modified gold electrode might be damaged when the potential exceeds this limit, accompanied by the appearance of the characteristic reduction peak of gold oxide.<sup>23</sup>

For TA  $pK_a = 5$  in solution,<sup>24</sup> the carboxylic terminus of the monolayer should be fully protonated at low pH and has a negative charge in neutral and basic solution. As a result, the response of  $\text{Fe}(\text{CN})_6^{3-}$  anion is effectively eliminated when the monolayer charge is negative at high pH where the carboxylic acid head group is dissociated. Fig. 1 shows series of CVs for the SAM modified gold electrode in the presence of 0.5 mmol/L  $\text{Fe}(\text{CN})_6^{3-}$ . As shown in Fig. 1, the peak current of  $\text{Fe}(\text{CN})_6^{3-}$  changes remarkably with bulk solution pH. The response of  $\text{Fe}(\text{CN})_6^{3-}$  can be observed only at low pH, while the current becomes significantly smaller at high pH. At low pH ( $< 4.0$ ), the CV exhibits well-defined wave, which indicates that the protonated end group of SAM hardly affects or inhibits the electron transfer of  $\text{Fe}(\text{CN})_6^{3-}$ . However, when pH value of bulk solution is over 5.6, the response of  $\text{Fe}(\text{CN})_6^{3-}$  gets smaller and the peaks are largely separated, implying the existence of great inhibition of SAM. Fig. 2 shows the dependence of peak current on the solution pH. The surface  $pK_a$  determined for TA is  $5.6 \pm 0.1$  from peaks of differential curves (dotted line).

We have recently put forward a theoretical simulation equation to relate the current response of gold electrode coated with an SAM terminated by  $-\text{COOH}$  group to the fractional extent of monolayer protonation.<sup>21</sup> By using the equation  $pK_a = \text{pH} + \log[(i_{\text{AH}} - i_{\text{A}^-}) / (i_{\text{A}^-} - i_{\text{A}^-}) - 1]$  where  $i_{\text{A}^-}$  and  $i_{\text{AH}}$  are currents of the probe on SAM fabricated by  $\text{A}^-$  and  $\text{AH}$  structures, respectively, a simulated curve can be obtained (solid line in Fig. 2) and the surface  $pK_a$  can be determined to be 5.6, which is well consistent with the experimental results.

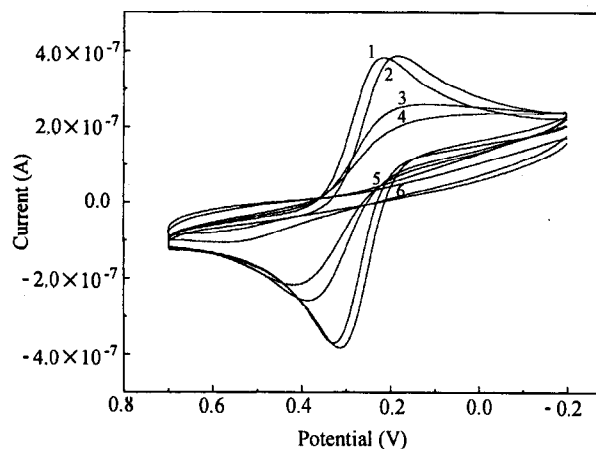


Fig. 1 pH dependence of cyclic voltammograms of 0.5 mmol/L  $\text{Fe}(\text{CN})_6^{3-}$  at TA SAM gold electrode; pH: (1) 2.9, (2) 3.5, (3) 4.0, (4) 4.6, (5) 5.0, (6) 5.6.

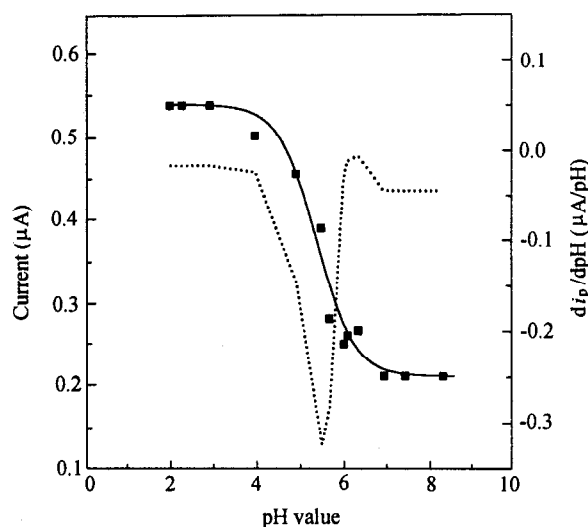


Fig. 2 Plot of current vs. solution pH for 0.5 mmol/L  $\text{Fe}(\text{CN})_6^{3-}$  at TA SAM gold electrode. The solid line is the simulated curve, and the dot line is the differential curve of experimental data.

#### EIS of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ at the SAM modified gold electrode in different solution

EIS is a powerful tool for the investigation of electrode process.<sup>25</sup> It is based on the measurement of the response of the electrochemical cell to a small amplitude

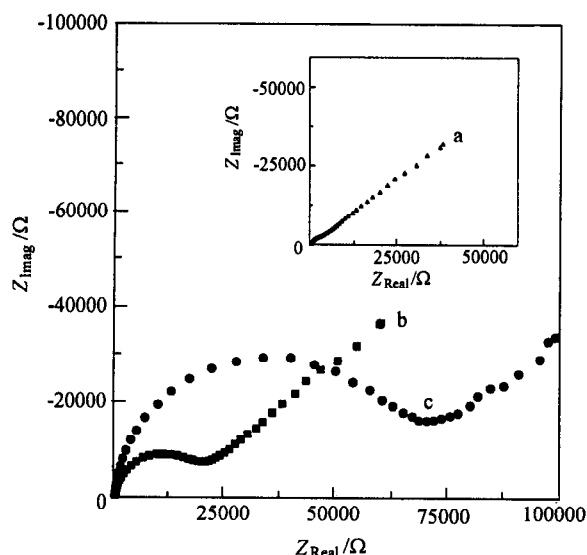
alternating potential. The possibility to vary the perturbing frequency within a very wide interval enables it to provide a wealth of information on the kinetic process as well as on ohmic resistance, double-layer capacitance and charge-transfer resistance.

Malinero and Calvo<sup>20</sup> have described theoretically

$$R_{CT} = \frac{RT}{n^2 F^2 A k^0 c^*} \exp \left[ -\frac{\chi}{RT} + \frac{[(z_R(1-\alpha) + z_O\alpha) z_A k c_T F^2 K_a^{-1} c_{H^+}]}{RT K_{A_{OH_p}} (1 \times K_a^{-1} c_{H^+})} \right],$$

which predicts a relationship among charge-transfer resistance ( $R_{CT}$ ), solution pH ( $c_{H^+}$ ) and surface  $pK_a$ .

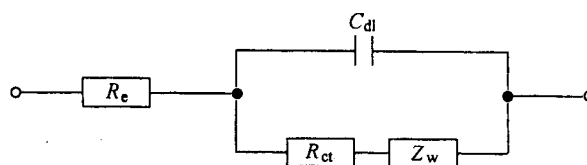
Fig. 3 illustrates the results of impedance spectroscopy on bare (a) and modified (b, c) electrodes in different pH solution which are measured at the formal potential of  $Fe(CN)_6^{4-/3-}$ . It can be seen from Fig. 3a that the bare gold electrode exhibits an almost straight line that is characteristic of a diffusion limiting step of the electrochemical process. With respect to the TA modified electrode, significant change in the impedance spectra is observed upon the change of solution pH (Fig. 3b, c). We can clearly observe that diameters of the semicircle parts increase with the increase of pH value of the solution, which means that the charge-transfer rate of  $[Fe(CN)_6]^{3-/4-}$  becomes reduced gradually. In



**Fig. 3** Complex-impedance plots of 0.5 mmol/L  $Fe(CN)_6^{3-/4-}$  on TA SAM in 0.2 mol/L PBS. (a) bare gold, pH 5.57; (b) Au-TA SAM, pH 5.57; and (c) Au-TA SAM, pH 7.53.

the dependence of the charge-transfer resistance as a function of solution pH on the basis of the Boltzmann surface concentration factor<sup>26,27</sup> and the potential distribution model of Smith and White<sup>27</sup> and that of Fawcett<sup>28</sup> for the Au-SAM-electrolyte interface. A simulated equation has been obtained as follows,

order to attain more detailed information about the impedance properties of the film, a modified Randle's equivalent circuit consisting of the bulk solution resistance  $R_e$ , the charge-transfer resistance  $R_{ct}$ , the electrical double-layer capacitance  $C_{dl}$  and the Warburg impedance  $Z_w$ , as shown in Fig. 4, can be chosen to fit the measured results.



**Fig. 4** Equivalent circuit of the EIS.  $R_e$  is the bulk solution resistance;  $R_{ct}$  is the charge-transfer resistance,  $C_{dl}$  is the electrical double-layer capacitance and  $Z_w$  is the Warburg impedance.

Fig. 5 shows the relationship between the charge-transfer resistance  $R_{ct}$  and the solution pH. It can be seen that  $R_{ct}$  increases with the increase of solution pH. The reason behind this can be explained as follows: At low pH, a protonated SAM is formed; at high pH, however, a negatively charged SAM is expected. Since redox couple  $Fe(CN)_6^{4-/3-}$  is highly negatively charged, the electrostatic repulsive interaction between redox couple and the SAM will result in the increase of  $R_{ct}$ , as shown in Fig. 5. This is in agreement with the increased irreversibility as seen in CV. The surface  $pK_a$  can be obtained to be  $5.8 \pm 0.1$  from the plot of  $R_{ct}$  versus solution pH.

The surface  $pK_a$  values measured by CV and EIS methods are both larger than the solution  $pK_a = 5$ .<sup>24</sup> This is in agreement with previous results for similar systems by other methods<sup>11-13</sup> where the surface  $pK_a$  is larger than the solution  $pK_a$ . This may be attributed to the

intermolecular hydrogen bonding among the surface molecules.<sup>11,29</sup>

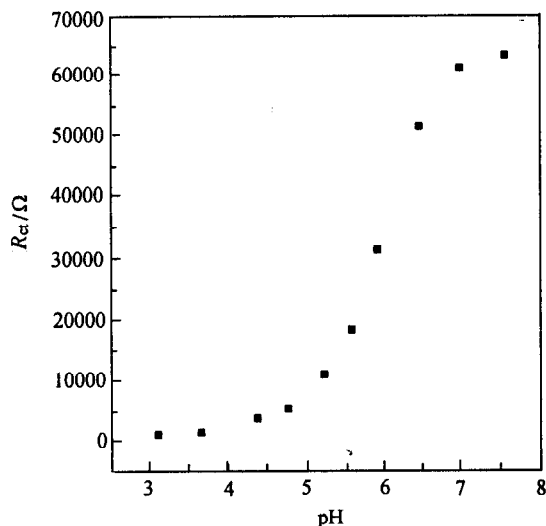


Fig. 5 Plot of  $R_{ct}$  vs . pH for 0.5 mmol/L  $\text{Fe}(\text{CN})_6^{3-/4-}$  in 0.2 mol/L PBS on TA SAM.

## Conclusion

We have studied the surface acid-base property of carboxylic acid-terminated self-assembled monolayers by cyclic voltammetry and electrochemical impedance spectroscopy. Thioctic acid was self-assembled on gold electrode and electron transfer between the bulk solution and the SAM modified electrode was studied at different pH using  $\text{Fe}(\text{CN})_6^{3-}$  as a probe. The surface  $\text{p}K_a$  of thioctic acid was determined by cyclic voltammetry and electrochemical impedance spectroscopy to be  $5.6 \pm 0.1$  and  $5.8 \pm 0.1$ , respectively. The surface  $\text{p}K_a$  obtained by the two methods is larger than the solution  $\text{p}K_a$ , which is consistent with previous reports. The results indicate that electrochemical method is a powerful tool to determine the surface  $\text{p}K_a$  of SAM.

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