

Measuring the Electronic Decay Constant of Alkanedithiols by Electrochemical Impedance Spectroscopy

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Several methods have been used for the measurement of the electronic decay constant (β) of organic molecules. However, each of them has some disadvantages. For the first time, electrochemical impedance spectroscopy (EIS) was used to obtain the β value by measuring the tunneling resistance through alkanedithiols. The tunneling resistance through alkanedithiols increases exponentially with the molecular length in terms of the mechanism of coherent nonresonant tunneling. β was 0.51 ± 0.01 per carbon.

The electronic decay constant, β , is a structure-dependent factor which can characterize the conduction properties of organic molecules with different structures. Various techniques including scanning tunneling microscope (STM), conducting-probe atom force microscope (CP-AFM), mercury/SAM junction, break junction are used to investigate the electron-transport properties of organic molecules. In STM,¹ owing to the uncertainty of the conduction of interested molecules, it is difficult to establish the location of the tip to molecules. If the tip is positioned above the films, an intervening vacuum gap formed between the tip and molecules will contribute to the junction resistance. In CP-AFM,² this problem is avoided. However, there still remains a problem in the reproducibility arising from many factors such as tip materials, ambient environment, and imaging force. As for mercury/SAM junction,³ the formed junction is mechanically unstable for the practical applications. Furthermore, there is a large discrepancy in the conductivity of single molecule between this method and other approaches. Break junction is a novel method for studying electron transport in a single molecule,⁴ but it has the drawback that interested molecules must be functionalized at both ends of the chains. Therefore, β values obtained by the four methods are different. It was reported that β values were 0.8 to 1.4 \AA^{-1} for alkanedithiols and 0.4 to 0.6 \AA^{-1} for oligophenylenedithiols.⁵ In this paper, the tunneling resistance through alkanedithiols was measured by electrochemical impedance spectroscopy (EIS). It is a more convenient, efficient and simple method to obtain the electronic decay constant.

Alkanedithiol-self-assembled monolayers (SAMs) were prepared by immersing the pre-treated gold electrode in the ethanol solution of alkanedithiols (1.0 mM) for 24 h. Then, the resulted electrode was sonicated with ethanol and washed thoroughly with ultrapure water. The prepared electrode was placed in the solution of $1.0 \text{ mM } [\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ for EIS measurements.

Figure 1 shows impedance plots of $1.0 \text{ mM } \text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ at the bare gold and alkanedithiol/gold electrode. As shown in plot a, the Nyquist diameter is quite small. The lin-

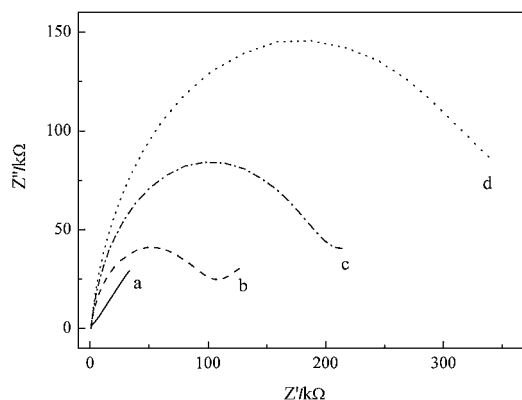


Figure 1. Nyquist plots of $1.0 \text{ mM } \text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ at (a) the bare gold electrode; (b) 1,6-hexanedithiol/gold electrode; (c) 1,8-octanedithiol/gold electrode; (d) 1,9-nonanedithiol/gold electrode with 0.1 M KCl as the supporting electrolyte.

ear part displayed in a large range of frequencies indicates the diffusion-limited step of the electrochemical process at the bare gold electrode. After alkanedithiols were self assembled on the gold electrode, the Nyquist diameters increase greatly. There are no linear parts at lower frequencies. It indicates that electrons diffuse much quickly from the solution to the surface of alkanedithiol/gold electrode, then alkanedithiols block the electron transport of the redox couple. The electron transport through alkanedithiol SAMs becomes to be the key step of the whole electrochemical process.

Figure 2 shows the S2p X-ray photoelectron spectroscopy (XPS) spectrum of a 1,9-nonanedithiol SAM on Au(111). Obviously, strong peaks at the binding energy (BE) from 162 to 165 eV are divided into two groups.⁶ One group at 162.2 and 163.4 eV is assigned to $\text{S}2\text{p}_{3/2}$ and $\text{S}2\text{p}_{1/2}$ arising from the spin-orbit splitting of the S2p. BE of $\text{S}2\text{p}_{1/2}$ is 1.2 eV higher than that of $\text{S}2\text{p}_{3/2}$. These are typical features of sulfur bound to the gold surface. The other group at 163.9 and 164.5 eV is assigned to the unbound thiol group. Therefore, only one of the sulfur atoms in the dithiol molecule is bound to the gold surface. It indicates that if electrons transfer from the electrolyte solution to the gold surface in the electrochemical process, it must tunnel through alkanedithiol SAMs via σ bonds in alkyl skeletons.⁷

Theoretical studies also prove that the electron-transport mechanism through SAMs is coherent nonresonant tunneling. The resistance increases exponentially with the tunneling length,⁸ which can be described as

$$R = R_0 \exp(\beta_N N). \quad (1)$$

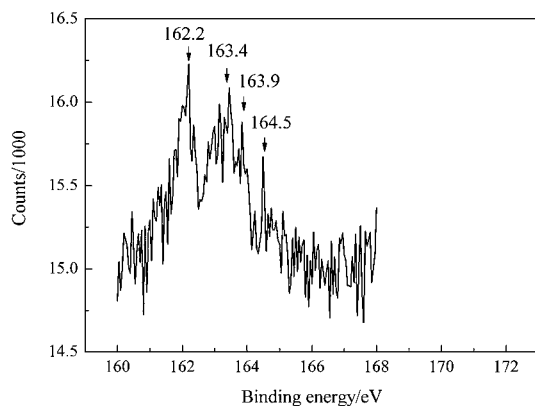


Figure 2. XPS spectrum in the S2p region of 1,9-nonanedithiol on the gold surface with two detectable S species.

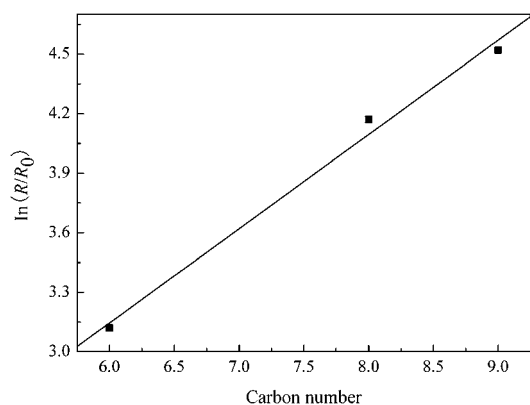


Figure 3. Logarithm of R/R_0 vs. carbon number of alkanedithiols.

where N is the molecular length which denotes the numbers of methylene groups in the alkyl chain, β_N is the electronic decay constant with the unit of 1/per carbon. R_0 is the effective contact resistance. In our experiment, it can be regarded as the resistance when the length of molecules is equal to zero, that is, the resistance through the bare gold electrode.

As shown in Figure 1, the tunneling resistance through alkanedithiols increases to hundreds of $k\Omega$ after the self-assembly and the electron-transport abilities of alkanedithiols decrease. The most important is that the tunneling resistance increases with the carbon numbers of alkanedithiols. The logarithm of the resistance through alkanedithiols is linear with the carbon numbers, from which β is calculated to be 0.51 ± 0.01 per carbon from the average of three repeated measurements (shown in Figure 3).

The β value of alkanedithiols in our experiment is much similar to those obtained with different methods. Cui et al.⁹ used

CP-AFM to probe electron transport through alkanedithiols linked between a gold substrate and gold nanoparticles. β_N was 0.57 ± 0.03 at zero bias. Haiss et al.¹⁰ studied molecules trapped between a gold substrate and a STM tip. The β_N value of alkanedithiols was 0.52 ± 0.05 . However, β_N measured by Xu and Tao⁴ with break junction was 1.0 ± 0.1 . A possible reason for the larger β_N is that more than one molecule formed junctions between STM tip and the gold substrate after the gold chain had been broken. As the length of alkanedithiols became longer, the interaction between molecules increased. Therefore, more alkanedithiol molecules might contribute to the tunneling resistance and resulted in a larger β_N . Compared with the methods mentioned above, our method is efficient, the detection process is not as tedious as those in break junction and STM which are repeated thousands of times. Furthermore, our method is more simple and convenient.

In summary, the structure and electron conduction properties of alkanedithiol SAMs were investigated by XPS and EIS. Alkanedithiols were self assembled on the gold surface through S–Au bond. The tunneling resistance increases exponentially with the length of alkanedithiols. The electronic decay constant of alkanedithiols was calculated to be 0.51 ± 0.01 per carbon. Electron transport through alkanedithiols is much faster than alkanethiols with the same carbon number.¹¹

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