Intermolecular Chain-to-Chain Tunneling in Metal−Alkanethiol−Metal Junctions

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Charge transport mechanism through molecular monolayers has been extensively studied for scientific and technological interests.[1] For example, the dominant charge transport mechanism in alkanethiol [$CH_3(CH_2)_{n-1}SH$] self-assembled monolayers (SAMs) is so-called through-bond tunneling, in which the current flows along the backbone of the all-trans alkyl chains via the overlapping σ-bonds.[2] This process is, therefore, independent of molecular tilt angles for a given molecular length. However, there is always intermolecular coupling through van der Waals interactions in an ensemble of the molecules. Such an intermolecular coupling can provide chain-to-chain tunneling (or through-space tunneling) pathways which involve lateral charge hopping between adjacent hydrocarbon chains.[2] In contrast to the through-bond tunneling, the chain-to-chain tunneling is sensitively dependent on the molecular tilt angle, which would be related to the tunneling distances.
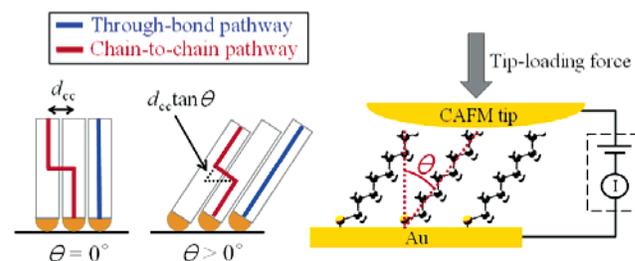
We report on a detail study of the intermolecular charge transport in alkanethiol SAMs formed in metal−molecule−metal junctions, particularly the molecular-tilt dependent chain-to-chain tunneling, using conducting atomic force microscopy (CAFM) where a tip-loading force is applied to the molecules so as to change the molecular tilt angle. The degree of molecular tilt under a tip-loading force is estimated, using mechanical contact theory. The tunneling currents in terms of the through-bond and chain-to-chain tunneling pathways were then measured as a function of the molecular tilt angle.

For our experiments, alkanethiol (from Sigma-Aldrich) SAMs of various molecular lengths were prepared on Au substrates. The metal−molecule−metal junctions were formed by placing a Au-coated AFM tip in the stationary point contact on alkanethiol SAMs under a controlled tip-loading force,[3] as shown in Scheme 1. All electrical measurements were carried out inside a nitrogen-filled AFM chamber. Experiment details are described in the Supporting Information.

We first investigated a force-dependent transport behavior in alkanethiol SAMs with a variable tip-loading force in the range from 1 to 30 nN. The current and the current density in the molecular junctions increased with increasing the tip-loading force (Figure S1 in the Supporting Information), which is consistent with previous results.[3] Several authors have suggested the existence of an ordered tilted-chain phase of alkanethiol SAMs on Au(111) within the loading effect applied by the tip[4] and most of the deformation under a tip-loading force leads to additional tilting of the molecules[5] even though gauche and other defect-related deformations might cause a small change in overall charge transfer.[6]

Molecular-tilt dependence on the intermolecular chain-to-chain tunneling is graphically illustrated in Scheme 1. The blue lines

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Scheme 1. Schematics Illustrating Tunneling Pathways through Alkanethiol SAMs and CAFM Method

indicate the through-bond tunneling pathway, whereas the red lines indicate the chain-to-chain tunneling pathway including the intermolecular charge hopping. A molecular tilt with angle θ results in a decrease in tunneling distance by $d_{cc} \tan \theta$ (where d_{cc} is the intermolecular distance) because the intermolecular charge-transfer takes place through the shortest pathway between adjacent alkyl chains.[2] Thus, the overall chain-to-chain tunneling distance is $d_m - d_{cc} \tan \theta + d_{cc}$ (where d_m is the molecular length).[2]

To study the chain-to-chain tunneling transport in alkanethiol SAMs, the model proposed by Yamamoto and Waldeck for molecular tunneling pathways was employed, which allows multiple intermolecular hopping.[7] For N times hopping, the chain-to-chain tunneling distance along the molecular chain tilted at angle θ is reduced by $Nd_{cc} \tan \theta$ and the total tunneling current density can be described as the sum of through-bond tunneling and chain-to-chain tunneling by[7]

$$J = J_0 \exp(-\beta_{tb}d_m) + J_0 \sum_{N=1}^{\frac{d_m \cos \theta}{d_{cc}}} \frac{n_s!}{(n_s - N)!N!} \exp(-\beta_{tb}(d_m - Nd_{cc} \tan \theta)) \times \exp(-\beta_{ts}Nd_{cc}) \quad (1)$$

where J is the current density through the alkanethiol SAMs. J_o indicates the current density without the SAMs, which can be obtained by extrapolating to zero length from a logarithm plot of current density versus molecular length (Table S1 in the Supporting Information). β_{tb} and β_{ts} are tunneling decay coefficients for through-bond and chain-to-chain tunneling, respectively. θ is the tilt angle of molecules with respect to the substrate normal, and a statistical factor n_s accounts for the increased number of pathways by the influence of intermolecular charge transfer and is assumed to be the same as the number of carbon atoms in the alkanethiol.[2,7] For alkanethiol SAMs, Slowinski et al. determined that $\beta_{tb} = 0.91$ Å^{-1} and $\beta_{ts} = 1.31$ Å^{-1}, respectively.[2]
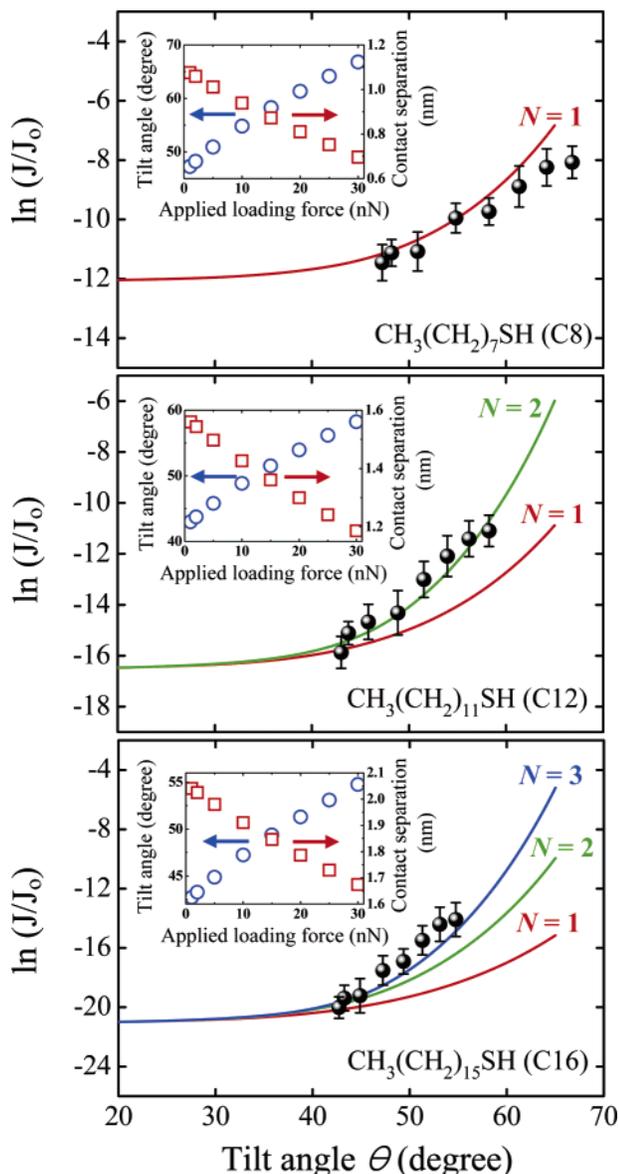
Figure 1. Semilog plots of normalized tunneling current densities as a function of the molecular tilt angle for different length alkanethiols. Insets show the relationship of molecular tilt angle θ, contact separation, and tip-loading force.

Figure 1 shows the results of the normalized tunneling current density (ratio J to J_o) as a function of molecular tilt angle induced by the tip-loading force for different length alkanethiols. The symbols are measured data and the solid curves are calculated using the multiple intermolecular hopping model (eq 1). To fit the measured data for the current density with eq 1, we obtained the relationship between molecular tilt angle, contact separation (distance between the tip and the Au substrate), and tip-loading force for each alkanethiol using the Johnson−Kendall−Roberts (JKR) mechanical contact theory[8] (see the Supporting Information for method detail), as shown in the insets of Figure 1.

It was estimated that the longer alkanethiol molecules were less tilted at the same tip-loading force. This is because the rigid longer alkyl chains stabilized by van der Waals force interactions can resist the tip stress more efficiently. This tendency is in agreement with AFM friction measurement results.[9]

Figure 1 shows that the experimental data obtained from CAFM measurements are consistent with the multiple intermolecular hopping model for the tilt angle dependence of alkanethiol tunneling. The best fits with the model are achieved with $N = 1$ for C8, $N = 2$ for C12, and $N = 3$ for C16, respectively. The fitted N value to each alkanethiol is reasonable agreement with the limitation $N \le d_m \cos \theta / d_{cc}$ in which total distance Nd_{cc} of the hopping cannot exceed the film thickness $d_m \cos \theta$.[7]

Here, we demonstrate that through-bond tunneling is the dominant transport mechanism in alkanethiols by investigating a dependence of current density on each tunneling distance for through-bond pathways (d_m) and chain-to-chain pathways ($d_m - d_{cc} \tan \theta + d_{cc}$; $N = 1$). In Figure S4 in the Supporting Information, it was evidently observed that the rate of current density increase for chain-to-chain pathways is smaller than that for through-bond pathways, meaning that through σ-bonds are more efficient tunneling pathways in alkanethiols than chain-to-chain pathways, which is consistent with previous results.[2,10]

In summary, the chain-to-chain tunneling in metal−alkanethiol−metal junctions was examined using CAFM. The results indicate that the tilt configuration of alkanethiol SAMs enhances the intermolecular charge transfer. As the molecular tilt angle increases with the tip-loading force, the chain-to-chain tunneling becomes significant, in addition to the already existing through-bond tunneling in overall transport.

Supporting Information Available: Experiment details; current and current density under variable tip-loading forces; the method for estimating the molecular tilt angle using the Johnson−Kendall−Roberts (JKR) contact model; dependence of current density on tunneling distances. This material is available free of charge via the Internet at http://pubs.acs.org.

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