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Gap size dependent transition from direct tunneling to field emission in single molecule junctions†

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***I*/*V* characteristics recorded in mechanically controllable break junctions revealed that field emission transport is enhanced in single molecule junctions as the gap size between two nanoelectrodes is reduced. This observation indicates that Fowler–Nordheim tunneling occurs not only for intermolecular but also for intramolecular electron transport driven by a reduced energy barrier at short tunneling distances.**

Over the past decade, fundamentals of charge transport through (bio-)molecules have been extensively investigated and several techniques have been developed to study the transport characteristics of metal–molecules–metal junctions.[1,2] Different charge transport mechanisms have been proposed for molecular junctions depending, for instance, on the electronic coupling between the metal and molecule, the intrinsic electronic structure of the molecule, and the applied bias voltage.[3,4] Beebe *et al.* demonstrated that metal–molecule–metal junctions can exhibit current–voltage characteristics that correspond to a transition from direct tunneling to field emission as the applied bias exceeds a threshold voltage.[5] The voltage at which this transition occurs (transition voltage V_T) is proportional to the energy offset between the metal Fermi level at zero bias and *e.g.* the highest occupied molecular orbital (HOMO). Based on a coherent Landauer approach, Huisman *et al.* calculated that V_T linearly correlates with the energy offset for small biases.[6] This feature allows probing of the effective energy barrier of charge transport by measuring V_T. The corresponding transition voltage spectroscopy remarkably advanced the measurement of the relative barrier height in molecular junctions.[6,7] Later, Wang *et al.* revealed that the transition voltage (V_T) is not fixed for a definite molecule. Using atomic force microscopy (AFM), they demonstrated that V_T shifts to lower voltages when the metal–molecules–metal junction was compressed.[8] Wang attributed the shifting of V_T to the enhanced interaction between parallel molecules (intermolecular electron transport) as the sandwiched molecules within the self-assembled monolayer were compressed. However, the relation between intermolecular interaction and charge transport mechanism is still under debate.[8–10]

In this communication, the charge transport characteristics of single molecule junctions instead of molecule layer junctions were investigated to evaluate the influence of neighboring molecules on the charge transport mechanism. Although the interaction between parallel molecules was unavailable in the single molecular junctions, shifting of V_T was surprisingly observed as the molecular junction was compressed. This indicates that the gap size of the junction rather than the intermolecular interaction strongly affects the electron transport mechanism. In order to realize stable single-molecule junctions, two nanoelectrodes with a precisely tunable gap are required. In the scope of this work, a mechanically controllable break junction (MCBJ) setup was used, Fig. 1. Here, a spring steel substrate carrying a lithographically defined wire containing a suspended nanometre sized constriction was mounted into a homemade three point bending apparatus. The two outer posts of the bending apparatus were fixed while the third one worked as a pushing rod movable in the Z direction. When the push rod displaced in the Z direction, a bending force was exerted on the substrate, which caused an elongation of the constriction until

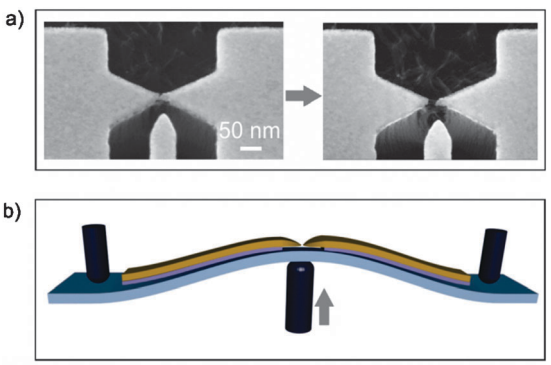

Fig. 1 Working principle of the mechanically controllable break junction (MCBJ). (a) Scanning electron microscopy images of the micro-fabricated MCBJ consisting of a freestanding metal bridge with a central constriction. (Left) before and (right) after breaking of the constriction. (b) Schematic of the MCBJ mounted into a three-point bending configuration. The push rod (piezo actuated) exerts a bending force on the substrate. The bending force breaks the metal bridge at the smallest constriction creating two separate nanoelectrodes.

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the bridge broke, resulting in two separated nanoelectrodes, see ESI†.[11]

After calibration of the molecule free junction, 1,8-octanedithiol (ODT) molecules were adsorbed and self-assembled on the gold wire from solution, dried and mounted into the MCBJ setup. The whole breaking process of the junction can be followed by monitoring the conductance of the molecular junction during the junction breaking process. At the beginning of the breaking process one can observe discrete conductance values which are multiples of G_0, Fig. 2. Further elongation of the junction results in a breaking of the gold–gold contact and a sharp drop in the conductance can be observed. After breaking the metal wire, two separated nanoelectrodes are generated. Due to the two thiol termini of ODT, the molecule is able to bind covalently to both generated nanoelectrodes and a metal–molecules–metal junction is formed. The molecular junction finally transforms into a single molecule junction as the gap size increases further. The last plateau (lowest conductance value) of the breaking trace can be assigned to the single molecule conductance. More than 200 metal–molecule–metal junctions were analyzed and the single molecule conductance was determined statistically to 2.5×10^{-4} G_0, which is consistent with earlier reports.[12] In contrast, the typical plateaus at values below 1 G_0 are absent for molecule free junctions.

To establish single molecule junctions, we stopped the push rod right before the conductance reached the value of 2.5×10^{-4} G_0 and waited until a stable junction was formed. Under these conditions, the gap size effect on the transport properties of a single molecule junction was investigated. Three sets of I/V curves were acquired at varied gap size, Fig. 3. Curves B and C were obtained after the gap size was reduced by 0.2 nm and 0.4 nm, respectively, based on curves A (conductance plateau at 2.5×10^{-4} G_0). The process of decreasing the gap size from one set to the other was performed in ten sub-steps at a fixed bias voltage of 13 mV. Only those data were further analysed where no sharp jumps or drops of the current were observed, indicating that no new

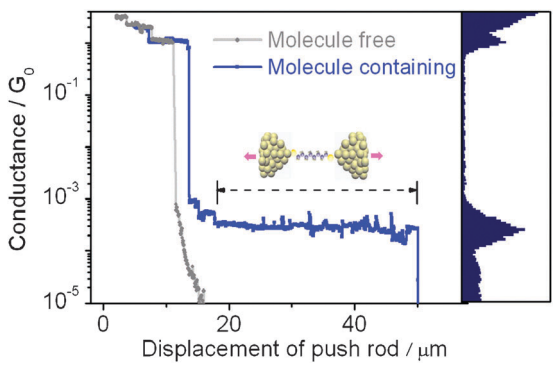

Fig. 2 The conductance of a molecule free junction and a molecule containing junction as a function of the push rod displacement. For the molecule containing junction, typical plateaus were observed after the breaking of the metal bridge, which indicates that a metal–molecules–metal junction was formed. For the molecule free junction, no pronounced plateau was observed at values below 1 G_0. The inset shows a stretched molecular junction before the final rupture of the junction. The conductance histogram shows a typical peak with a maximum at 2.5×10^{-4} G_0.

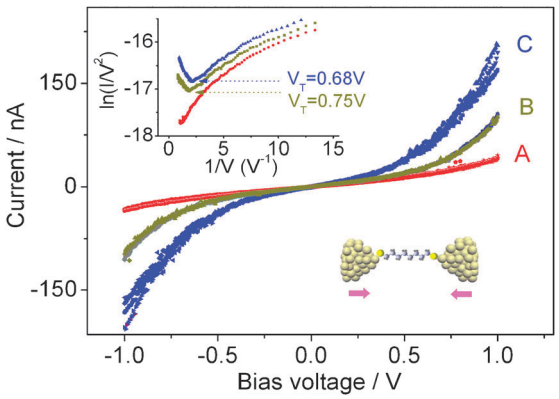

Fig. 3 I/V curves of single molecule junctions with three different gap sizes. Curves B and C were recorded after the gap size was decreased by approx. 0.2 and 0.4 nm based on curves A. The inset shows the corresponding $\ln(I/V^2)$ *versus* $1/V$ characteristics. An inflection point can be observed, which shifts to lower biases as the gap size decreases.

bonds between the molecule and electrode were formed or broken. $\ln(I/V^2)$ *versus* $1/V$ curves of three different gap sizes are shown in the inset of Fig. 3. At the initial gap size (red curve), the $\ln(I/V^2)$ *versus* $1/V$ plot exhibits no significant voltage dependence. The curve reveals that only the direct tunneling mechanism was present within the bias range between −1 V and 1 V. After the junction was compressed by approximately 0.2 nm, a transition from direct tunneling to field emission occurred at a transition voltage of 0.75 V. An additional decrease of the gap size by 0.2 nm led to a further shift of the transition point towards lower voltages, now 0.68 V. The inset picture explicitly demonstrates that the energy barrier of the junction decreases as the gap size decreases. In other words, field emission is enhanced as the gap size is reduced in the single molecule junction.

It should be noted that intermolecular tunneling between parallel molecules was unprobable since the junction was bridged by only a single molecule, and adjacent molecules were linked to only one of the two facing nanoelectrodes. Thus, an explanation that attributes the enhanced field emission only to changed transport pathways including intermolecular electron transport (chain-to-chain tunnelling in parallel molecules) seems to be inappropriate. Also direct tunneling between the electrodes is leading to a rather linear increase of the tunneling current within the investigated bias regime (0 V to 1 V)[13] and cannot explain the observed strong nonlinear increase of the I/V curves for the molecular junction manifested in V_T below 1 V. In order to further evaluate the role of intermolecular charge transport, an additional experiment was performed where the number of trapped molecules was altered, but the final gap size was kept mainly unchanged. For this purpose, the junction was gently compressed and relaxed, see ESI.† During each approaching and withdrawing process there was a certain probability that either new bonds between molecules and electrodes were formed or existing bonds were broken. Therefore, it can be assumed that the two nanoelectrodes were bridged by different numbers of molecules after this procedure, although the final gap size was nearly the same. We found that 90% of the I/V characteristics fall into three distinct sets of curves (see Fig. 4, for details and reproduced data see ESI†).

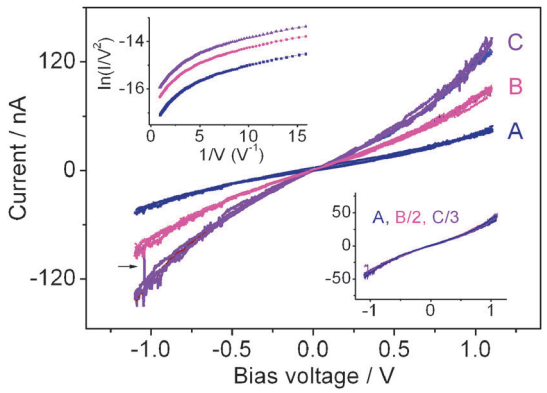

Fig. 4 I/V curves of the molecular junction with varied number of trapped molecules at a fixed gap size. The measured I/V responses fall mainly into three sets of curves. The sets represent multiples (B = 2, C = 3) of the fundamental characteristics (A = 1). The arrow indicates the change of the number of trapped molecules in the junction. Top inset: no field emission was observed independent of the number of entrapped molecules. Bottom inset verifies that the I/V curves are multiples of each other.

The three sets represent multiples of each other and can be deduced from the (fundamental) characteristics of a single molecule junction. It can be assumed that each set of curves corresponds to nanoelectrodes bridged by 1, 2, or 3 molecules, respectively. The inset in Fig. 4 shows that no field emission was observed for all three sets of I/V characteristics within the bias window between −1 V and +1 V. A correlation between the transition voltage and number of molecules in the junction was not found for this type of molecule.

Several aspects have to be considered for the explanation of the enhancement of field emission in single molecule junctions if intermolecular transport can be neglected. At first, according to the full Simmons model, V_T will decrease as the tunneling distance decreases for narrow gaps, if one takes the image potential into account.[6] However, the Simmons model is based on a rectangular barrier modified by an image potential, which does not in total take the particularities of molecules into account like molecule–electrode coupling (see below). Empirical models based on a coherent Landauer approach are in good agreement with V_T characteristics at tunneling distances larger than 8 Å,[5,6] but deviate for smaller gaps, see data reported here and Wang *et al.*[8] A possible explanation can be the increasing electric field for decreasing gap sizes. A change of the electrode distance by few angstroms for sub nm gaps will result in a considerable alternation of the electric field strength in the junction, see ESI.† Density functional theory calculation showed that increasing electric fields can alter the electronic structure of molecules and reduce their HOMO–LUMO gaps.[14,15] Following this idea, one can assume that a decrease of the gap size leads to an enhancement of the electric field, resulting in a decrease of the tunneling barrier height. A smaller barrier height causes a shift of the transition voltage to lower bias voltages, which can be observed as an enhancement of field emission.

Another factor that should be considered is the junction distortion caused by their mechanical compression. When the gap size between the two nanoelectrodes is reduced, the sandwiched molecule in the junction experiences a certain compression force. The compression force will change the metal–molecule contact, which will affect the electronic structure of the junction, including the spatial distribution of the frontier orbits, the HOMO–LUMO gap, and transmission function.[16] This reconfiguration of the electronic structure can affect the electron transport characteristics and contribute to the enhanced field emission.

In summary, charge transport at the single molecule level was investigated by means of high stability mechanically controllable break junction experiments. Although the transport between parallel molecules was unprobable in the single molecular junction, a shifting of V_T was surprisingly observed as the molecular junction was compressed. I/V measurements with different numbers of molecules in the junction at a given gap size revealed that intermolecular electron transport between adjacent molecules was of minor importance and alkanedithiol molecules can be considered as individual transport channels. The presented observations lead to the conclusion that the distance change between the electrodes and associated alternations of the molecular electronic structure rather than intermolecular tunneling result in the enhancement of field emission for alkanedithiols.

Notes and references

1 (*a*) B. Q. Xu and N. J. Tao, *Science*, 2003, **301**, 1221; (*b*) E. Lortscher, H. B. Weber and H. Riel, *Phys. Rev. Lett.*, 2007, **98**, 176807.
2 (*a*) Y. Liu, A. Offenhausser and D. Mayer, *Angew. Chem., Int. Ed.*, 2010, **49**, 2595; (*b*) Z. Yi, S. Trellenkamp, A. Offenhäusser and D. Mayer, *Chem. Commun.*, 2010, **46**, 8014.
3 (*a*) R. J. Nichols, W. Haiss, S. J. Higgins, E. Leary, S. Martin and D. Bethell, *Phys. Chem. Chem. Phys.*, 2010, **12**, 2801; (*b*) W. Y. Wang, T. Lee and M. A. Reed, *Rep. Prog. Phys.*, 2005, **68**, 523; (*c*) L. A. Zotti, T. Kirchner, J. C. Cuevas, F. Pauly, T. Huhn, E. Scheer and A. Erbe, *Small*, 2010, **6**, 1529.
4 (*a*) H. B. Weber, J. Reichert, F. Weigend, R. Ochs, D. Beckmann, M. Mayor, R. Ahlrichs and H. von Lohneysen, *Chem. Phys.*, 2002, **281**, 113; (*b*) J. C. Genereux and J. K. Barton, *Chem. Rev.*, 2010, **110**, 1642; (*c*) Q. Lu, K. Liu, H. M. Zhang, Z. B. Du, X. H. Wang and F. S. Wang, *ACS Nano*, 2009, **3**, 3861.
5 J. M. Beebe, B. S. Kim, J. W. Gadzuk, C. D. Frisbie and J. G. Kushmerick, *Phys. Rev. Lett.*, 2006, **97**, 026801.
6 E. H. Huisman, C. M. Guedon, B. J. van Wees and S. J. van der Molen, *Nano Lett.*, 2009, **9**, 3909.
7 (*a*) J. M. Beebe, B. Kim, C. D. Frisbie and J. G. Kushmerick, *ACS Nano*, 2008, **2**, 827; (*b*) P. W. Chiu and S. Roth, *Appl. Phys. Lett.*, 2008, **92**, 063511.
8 G. Wang, T. W. Kim, G. Jo and T. J. Lee, *J. Am. Chem. Soc.*, 2009, **131**, 5980.
9 X. D. Cui, A. Primak, X. Zarate, J. Tomfohr, O. F. Sankey, A. L. Moore, T. A. Moore, D. Gust, G. Harris and S. M. Lindsay, *Science*, 2001, **294**, 571.
10 J. G. Kushmerick, J. Naciri, J. C. Yang and R. Shashidhar, *Nano Lett.*, 2003, **3**, 897.
11 C. Zhou, C. J. Muller, M. R. Deshpande, J. W. Sleight and M. Reed, *Appl. Phys. Lett.*, 1995, **67**, 1160.
12 B. Q. Xu, *Small*, 2007, **3**, 2061.
13 M. L. Trouwborst, C. A. Martin, R. H. M. Smit, C. M. Guedon, T. A. Baart, S. J. van der Molen and J. M. van Ruitenbeek, *Nano Lett.*, 2011, **11**, 614.
14 H. Basch and M. A. Ratner, *J. Chem. Phys.*, 2004, **120**, 5761.
15 R. R. Kan, H. M. Liu, Y. F. Ye, P. Li, X. Yin and J. W. Zhao, *Acta Phys. Chim. Sin.*, 2007, **23**, 671.
16 (*a*) W. Gao, M. Zhao and Q. Jiang, *Appl. Surf. Sci.*, 2009, **255**, 9259; (*b*) T. Frederiksen, C. Munuera, C. Ocal, M. Paulsson, D. Sanchez-Portal and A. Arnau, *ACS Nano*, 2009, **3**, 2073.

