学校编码：10384　　分类号_____密级 _____

学号：20520100153666　　UDC _____

厦门大学

博 士 学 位 论 文

金属原子线和单分子结的 STM 纳米构筑及量子输运

Metal Atomic Wires and Single Molecular Junction: Nanoconstruction by STM and Their Quantum Transport

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论文提交日期：2015 年 9 月
论文答辩时间：2015 年 11 月
学位授予日期：2015 年 月

答辩委员会主席：_____

评 阅 人：_____

2015 年 9 月

Metal Atomic Wires and Single Molecular Junction: Nanoconstruction by STM and Their Quantum Transport

A Dissertation Submitted for the Degree of Doctor of Philosophy

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September, 2015

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摘 要

金属原子线和金属-分子-金属结(分子结)等异质结是纳/分子电子学中研究最广泛的基本单元，它们表现出特殊的量子输运性质，如何构建这些分子尺度的异质结、表征其电荷输运行为并且探究调控电导的因素，是该领域当前的重要研究内容。STM 裂结法（Scanning tunneling microscope break junction, STMBJ）是目前研究金属原子线和分子结的成熟方法之一，不仅可以快速重复地构建异质结，得到大量的可用于统计分析的电导曲线，也可以对异质结进行 $I-V$ 表征。本论文主要运用 STMBJ 技术，从构建金属原子线到金属-分子金属结，研究金属原子线的量子电导和一系列分子结的电荷输运行为；在此基础上引入光激励系统，探索光与分子结相互作用及光对分子结电学性质的影响。主要研究内容和结论如下：

1、基于 STMBJ 仪器平台的完善。在商品化仪器上与陈招斌博士(厦门大学)合作改造了 STM 扫描器前置放大电路，扩展测量数据采集的通道数目和电流采集范围，电流检测灵敏度可达 10 pA/V ~ 5 μA/V，满足金属量子电导和分子电导同时检测的需求，系统可靠性得到 4,4'-联吡啶分子电导的验证，所得电导值与大部分研究组的结果一致；在此基础上，搭建光路系统和观察系统，可以进行激光作用下的实验，可用于分子结的光调控研究。该平台为构建和研究异质结奠定了坚实基础。

2、发展了基于 jump-to-contact 机制的电化学 STMBJ 方法，用于构建 Ag 金属原子线并研究其量子电导。通过对比 jump-to-contact 和 crash-to-contact 两种机制下构建的银原子线及其电导值的区别，前者构筑的原子线具有晶形结构，Ag 量子电导为 1、2、3 G_0（$G_0 = 2e^2/h$）；后者构建的 Ag 原子线结构不确定，检测到的 Ag 量子电导为 1、2.5、4 G_0，其中出现分数倍的量子电导值，揭示了量子电导与原子线结构之间的关系。

3、探讨分子结的影响因素。使用 STMBJ 或者 I(s)技术研究了吡啶基功能化的分子、对环芳烷分子、钌金属有机化合物分子、蒽醌类分子的电荷输运行为，这些分子可作为潜在的分子器件或者作为分子器件的构筑模块(building block)。其中包括：(a) 对比了金、银电极对吡啶基分子电导测量的影响，Ag 电

极比 Au 电极测得的分子电导值低，但是分子结的拉伸长度更长。(b) 具有大 π 键的卟啉衍生物的 2D 电导统计图中，观察到分子结拉伸过程中分子电导与构型之间的变化关系。(c) 金、铂两种电极测试了 [2,2]-paracyclophanes 分子内 π-π stacking 的电导性质，在 Au 电极上测得 7.5 mG_0，Pt 电极上测得 0.4 G_0，较大的电导值表明[2,2]-paracyclophanes 分子内的 π-π stacking 对电荷的输运是十分有利的。(d) 在电化学体系下研究了不同取代基位置的蒽醌衍生物分子，由于分子具有不同长度和共轭性，单分子电导分别为：14aq (4.0 nS) > 15aq (2.1 nS) > 26aq (0.68 nS)。同时，蒽醌分子具有较好的氧化还原可逆性，在还原状态下形成共轭性更好的带酚羟基的分子 14aq_r、15aq_r 和 26aq_r，电导值分别增加到 300、145 和 55 nS。蒽醌衍生物分子还原态/氧化态的开关比大约在 70~80 倍，蒽醌基团具有分子开关的潜在利用价值。(e) 运用 I(s)方法研究了一系列三联吡啶配位的钌金属有机化合物分子电导，实验方法获得的分子长度比实际分子长度来得短，这与锚定基团甲硫基的接触构型有关，也与分子在两电极之间有一定的倾斜角、以及分子还没有完全拉伸分子结即断裂有关。虽然这一系列分子具有单金属中心和双金属中心两类，然而他们的分子电导与分子长度的关系依然呈现指数衰减关系，衰减系数为 1.5 nm^{-1}，这类分子的电荷输运属于隧穿机理。

4、光对分子结的影响。基于光耦合 STMBJ 研究表面等离激元(SPR)驱动表面催化反应，提出了光催化辅助构建分子结的方法，在针尖-基底耦合以及激光作用在对巯基苯胺（PATP, 0.3 mG_0）体系中检测到其偶联产物偶氮苯衍生物的单分子电导（DMAB, 4.3 mG_0），从单分子水平深入理解 SPR 驱动的表面催化反应过程。另外，还发现 DMAB 分子中的 N=N 双键在紫外光照射下发生顺反异构，异构体具有不同的电导值，开关比约为 3。

5、“自下而上”构建分子结的方法。自下而上是提高器件集成度，实现分子器件功能的有效途径，本论文利用电化学还原重氮盐前驱体的方法构建Au-C连接的分子层，再通过后续的表面Sonogashira反应修饰锚定基团，最后构建一端Au-C共价连接另一端乙酰巯基（或者二茂铁基团）连接的分子结，I(s)方法测得分子结电导分别为3.0和4.4 nS。另外，在双端硫醇分子层上还原氯金酸形成金属纳米岛(~10 nm)-分子层-金属这样的分子结，对该体系做了STM、XPS表征和IV测试，该方法避免了电化学还原导致部分金属穿透分子层而短路的问题。

关键词：分子电子学；银原子线；分子结；量子输运；扫描隧道显微镜

Abstract

Atomic wire and metal/molecule/metal junctions (molecular junctions) are the basic units of molecular electronic. Such heterojunctions show special features of quantum transport. How to build those molecular heterojunctions and to characterize their charge transport and explore the influencing factors are the currently important research contents in the field of molecular electronics. The technology of scanning tunneling microscope break junction (STMBJ) is one of the most extensively applied methods for construction of metal atomic wire and molecular junctions. STMBJ can quickly and repeatedly construct the heterojunctions and collect a lot of conductance curves for statistical analysis. Furthermore, STM also can be used to carry out the I-V characterization. In this thesis, by using STMBJ technique, we study the quantum conductance of silver atomic wire and a series of molecular junctions. Furthermore, by combining a laser excitation system to the STMBJ setup, we explore the interaction between light and molecular junctions and study an SPR-driven surface catalytic reaction. The main research contents and conclusions are outlined as follows:

1. The improvement of the platform based on STMBJ setup. In collaboration with Dr. Zhaobin Chen (Xiamen university), we extend on a commercial STM instrument, the data acquisition channel and current collection range by changing the preamplifier circuit so that the current detection range can be enlarged up to 10 pA/V ~ 5 μA/V, meeting the testing requirements of for recording the conductance of both metal atomic wire and molecular junction in one experiment. By using 4, 4 '-pyridine molecules, we tested and verified the reliability of the system, the results being consistent with most of the other groups. Thereafter we update the STMBJ setup by combining optical system and observation system. The updated platform can operate under laser irradiation, which lay a foundation for construction of heterojunctions and for study of interactions between light and molecular junctions.
2. Development of the STMBJ method based on jump-to-contact mechanism by electrochemical means for the construction and study of the quantum transport of Ag atomic wire. By comparing the methods jump-to-contact STMBJ and crash-to-contact STMBJ, it is found that the former method creates well-defined crystalline atomic wire and Ag quantum conductance of 1, 2 and 3, integer times of G_0 (G_0 =

$2e^2/h$), can be obtained; While the latter method creates defective Ag atomic wire andthe Ag quantum conductance at 1, 2.5, 4 G_0, which are not multiples of quantum conductivity value. The results reveal the relationship between the atomic structure and quantum conductance.

3. To explore the influencing factors of molecule conductance. By using STMBJ or I(s) techniques charge transport of molecular junctions are studied including the pyridyl molecules, the paracyclophanes, ruthenium metal organic compounds and anthraquinones. Those molecules can be used as a potential building block for molecular devices. (a) We use gold and silver electrodes for testing pyridyl molecules electron transport behavior. It is found that the conductance value is lower by Ag electrode than by Au electrode, but the step length measured by Ag electrode is longer than by Au electrode. (b) The 2D conductance histogram of porphyrin derivatives shows the relationship between conductivity and configuration during the stretching process. (c) The conductance of [2,2]-paracyclophanes measured by Au and Pt electrodes are relatively high, which are 7.5 mG_0 and 0.4 G_0 respectively, revealing that charge transport is very good in intramolecular π-π stacking of [2,2]-paracyclophanes. (d) The conductance of anthraquinone derivatives molecules in electrochemical environment are also studied. The molecules have different substituent positions, leading to different length and conjugation, their single molecule conductance are respectively: 14aq (4.0 nS) > 15aq (2.1 nS) > 26aq (0.68 nS). Anthraquinones at reducing state are better conjugated and their conductance value increase to 300 nS (14aq_r), 145 nS (15aq_r) and 55 nS (26aq_r) respectively. Their conductance ratio of reduction /oxidation are about 70 ~ 80 times. (e) By using I(s) method, a series of ruthenium metal organic compounds are studied. Although this series of molecules have single or double metal centers, the relationship of their molecular conductance and molecular length is still rendering exponential decay, the decay coefficient β is 1.5 nm^{-1}, indicating their charge transport matching the tunneling mechanism.
4. Investigation of the influence of light on the molecular junction. We present a mult-functional platform to study the plasmon-driven chemical reactions and dynamics at single-molecule level. We can detect the product of p,p'-dimercaptoazobisbenzene (DMAB, 4.3 mG_0) on a p-aminothiophenol (PATP, 0.3 mG_0) modified Au(111) surface under laser induced plasmon-driven chemical reaction. The tip - substrate coupling interaction with p-polarized laser can

produce strong plasmon that effectively drives PATP to be oxidized to DMAB. On the other hand we found that there is N=N double bond in DMAB molecule which becomes cis-trans isomerism under UV irradiation, the conductance ratio of the cis/trans isomers is about 3.

5. Development of "bottom up" construction of molecular junctions based on molecular assembly. (a) By electrografting diazonium salt on Au(111) surface, a molecular layer with Au-C binding is formed. A subsequent surface Sonogashira reaction modification of the end group of the asprepared molecular layer leads to attachment of, forming a molecular junction with Au-C contact and acetyl thiol (or ferrocene) end group. The molecular conductance measured by I(s) method were 3.0 and 4.4 nS. (b) Octdithiol modified Au(111) immersion in $HAuCl_4$ solution form metallic nanoisland (~10 nm)/octdithiol/metal junction, characterization of the structure by STM, XPS and I-V test. This method is much more convenient and avoid damage of molecular layer and short circuit problem compare with the electrochemical reduction.

Keywords: molecular electronics; Silver atomic wire; Molecular junctions; Quantum transport; Scan tunneling microscopy (STM)