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论文题目: 扫描隧道显微术在特殊纳米体系中的应用与发展

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中 文 摘 要

扫描隧道显微镜的原子操控、高分辨结构表征与电子态表征等能力使得它在表面科学很多体系中得到了充分广泛的应用。然而对于一些特殊体系, 例如对称性低的分子和高速运动的吸附原子, 通常使用的STM方法在确认其结构或测量其运动速度方面显得力不从心。

本论文将利用扫描隧道显微镜(STM)分别从几个典型的人们所关注的热点问题出发, 发展一些新的技术和方法, 拓展扫描隧道显微镜在表面科学中的研究能力, 并试图解决一些困难而有意义的科学问题。

本论文按以下几部分展开讨论:

在第一章, 我们简要介绍了扫描隧道显微镜的发明、发展、技术关键以及其在原子分子成像、操纵和在纳米电子学研究当中获得的重要成果。作为对后面几章内容的铺垫, 这里我们着重介绍了STM的工作模式及这些工作模式的特点。

在第二章中我们对单个铜族贵金属原子在Si(111)表面的吸附与扩散运动从吸附位置、扩散速度和扩散路径三个方面进行比较全面的研究。半导体材料硅的(111)表面存在着 7×7 重构, 这种重构自然形成了一个原子栅栏, 可以限制一个金属原子在它半个原胞内跳跃(扩散)。常温下, 这种跳跃很快($>10000\text{Hz}$), 整个半原胞内都能看到它的身影, 于是常有人误认为这是一个团簇。我们的降温实验确定了这只是一个单原子的事实, 并且结合理论计算方法给出了低温下铜族金属原子在Si(111)- 7×7 表面的吸附位置。这个吸附位置与STM观察到的亮点位置不一致, 理论上解释了这种不一致, 并重现了STM图像。对于金属原子的快速扩散运动, 我们利用STM设计了一种全新的方法对其扩散系数进行了测量, 这种方法比已有的STM方法至少快3-4个量级, 并且很容易进行进一步扩展, 大大提高了STM对表面扩散现象的研究能力, 并使其测

量快速的氢原子量子扩散运动成为可能。

富勒烯的球形笼状结构引起人们的极大兴趣，对它们的结构、输运和应用都有大量的研究。在第三章中我们利用STM 结合密度泛函理论计算方法研究了金属包合富勒烯 (Dy@C-82) 分子吸附于 $\text{Si}(111)-(\sqrt{3}\times\sqrt{3})\text{Ag}$ 表面上的局域电子结构，特别是金属-碳笼杂化轨道。实验与理论的相结合有力的说明了金属原子除了与碳笼间有电荷转移外，还存在着轨道杂化相互作用。对照理论与实验的结果可以确定出碳笼内部原子的位置和整个分子吸附于表面时的吸附取向。在这一章里我们还用STM 仔细研究了吸附在Au 表面的富勒烯二聚物分子 C-120，首次获得了这种分子的化学键分辨的STM 图象，并第一次直接从图像上确定出C-120 分子的结构。

最后，我们把目光转向纳米粒子。在第四章中，我们发展了一种新的化学制备方法，成功合成了尺寸可控的晶态和非晶态Pd 纳米颗粒。之后，我们利用STM 对晶态与非晶态的Pd 纳米粒子的电子结构进行了比较研究。结果显示，尽管晶态的纳米钯颗粒已经表现了理论上该有的量子效应，但仅仅结构不同的非晶态同尺寸的纳米钯颗粒却保持了其经典的输运性质。理论分析表明，这是由于原子无序化造成了非晶态Pd 颗粒的能级展宽，直接导致了对其量子限域效应的抑制。这个结果说明仅仅减小尺寸还不足以使物体发生量子化转变，结构的影响也是至关重要的。进一步利用STM 对晶态钯颗粒进行操控实现串连耦合，在其I-V谱中观察到类似于分子体系的负微分电阻效应，从实验上证明极小尺度的金属量子点由于存在分立能级结构，也可以用于构造负微分电阻器件。

关键词： 扫描隧道显微术 表面扩散 富勒烯 纳米粒子

Applications and Extensions of Scanning Tunneling Microscopy in Specific Nano Systems

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ABSTRACT

Scanning Tunneling Microscope (STM) has been widely used in many areas since its invention. But for some specific nano systems, such as low symmetrical molecules, or fast moving atoms, the common STM technologies cannot deduce the structure or measure their diffusion frequency. In this dissertation, we have developed and demonstrated some new technologies/methods to extend the power of STM, and solved such specific problems.

In Chapter 1, we briefly introduce the development of STM and its basic principle. Here we mainly discussed the working modes and their differences. We also introduce the applications of STM in the imaging, atom operating and nanoelectronics.

In chapter 2, by confining a diffusion atom in a nanometer region using surface potential heterogeneity, we have successfully employed a time-dependent tunneling spectroscopy to quantitatively study its random motion. A hopping rate in the range of 1 - 10000 Hz, ~3 orders of magnitude faster than those accessible by the existing diffusion methods based on scanning tunneling microscopy, was demonstrated for single Cu, Ag and Au atoms diffusing in the half unit cell of Si(111)-7×7. Our technique is potentially useful to detect fast diffusion processes such as H quantum diffusion at atomic scale. On the other hand, using scanning tunneling microscopy and first principles calculations, the adsorption sites of single Cu, Ag, and Au atoms on the Si(111)-7×7 surface have been systematically investigated and identified. Despite their monovalence, these atoms were found to adsorb at high coordination sites, seeking to saturate the maximum number of dangling bonds. The stable adsorption sites were further observed to be distinctly different in the faulted and unfaulted half unit cells, showing an asymmetry that has never been observed for many other adsorbates.

In chapter 3, the local structural and electronic properties of individual metallofullerenes are studied using scanning tunneling microscopy, scanning

tunneling spectroscopy, and theoretical simulations. The energy-resolved metal-cage hybrid states of a single endohedral metallofullerene Dy@C₈₂ isomer I have been spatially mapped, supporting a complex picture consisting of the orbital hybridization and charge transfer for the interaction between the cage and the metal atom. The relative position of the encapsulated Dy atom inside the cage and the molecular orientation on the surface have been inferred by comparing the experimental results with theoretical simulations. The combined technique provides promising applications in the fields of *in situ* characterization and diagnostics of metallofullerene-based nanodevices

In chapter 4, Size-selectable ligand-passivated crystalline and amorphous Pd nanoparticles (< 4 nm) are synthesized by a novel two-phase process and verified by high-resolution transmission electron microscopy. Scanning tunneling spectroscopy performed at 5 K on these two types of nanoparticles exhibits clear Coulomb blockade and Coulomb staircases. Size dependent multipeak spectral features in the differential conductance curve are observed for the crystalline Pd particles but not for the amorphous particles. Theoretical analysis shows that these spectral features are related to the quantized electronic states in the crystalline Pd particle. The origination of the negative differential resistance effect in series-coupled crystalline Pd particles is also attributed to the discreteness of energy levels of both the coupled Pd particles. The suppression of the quantum confinement effect in the amorphous particle arises from the reduction of the degeneracy of the eigenstates and the level broadening due to the reduced lifetime of the electronic states.

Key words: Scanning Tunneling Microscopy, Surface diffusion,
Fullerene, Nanoparticles