Tuning the electronic properties of metal surfaces and graphene by molecular patterning
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Chapter 1

Introduction

1.1 Motivation
Curiosity is always the best teacher. The simple desire to explore the unknown is the ultimate force that has been and still is driving the progress of human civilization. “What is the smallest unit of matter?” This question has puzzled mankind for thousands of years. In the fifth century B.C., the Greek philosopher Leucippus claimed that when matter is divided into smaller pieces, at some point it will reach the smallest unit that still retains the properties of that substance. This indivisible unit is called “atom”. Even though the first idea of atomism emerged more than 2000 years ago, the scientific understanding of the concept “atom” and its structure was only realized around the middle of the 20th century. The great progress in quantum mechanics has made it possible to understand the phenomena occurring on the atomic scale. A very few people started to realize that “there’s plenty of room at the bottom” [1], which is nowadays seen as the starting point for the age of nanoscience.
Since the length scales of atoms and molecules are on the nanoscale, nanoscience can also be viewed as the study dealing with the basic building blocks of matter. At the nanoscale, quantum effects start to dominate the properties of materials resulting in unique phenomena which offers the possibility to design materials with novel properties which is not feasible when working with bulk materials. The ultimate goal of nanoscience is the production of materials with advanced properties by controlling the manufacturing process with nanoscale precision. To achieve this goal, two
main approaches have been developed: the top-down approach and the bottom-up approach. In the top-down approach, large pieces of materials are reduced to smaller dimensions to fabricate devices with specific properties, just like carving a statue out of a big block of marble. In the bottom-up approach, building blocks at the atomic or molecular scale are assembled into larger objects in order to generate devices with tailored functions, just like building a wall with pieces of bricks. Nowadays, the top-down approach is already widely used in industrial processes. An example of a top-down approach is lithography [2], which is the dominant technique used to produce integrated circuits in the semiconductor industry. To meet the demand of the rapid growing semiconductor market, more and more transistors need to be integrated. In 1965, Gordon Moore made a prediction that the number of transistors on the integrated circuit with a defined area doubles approximately every two years [3]. More transistors would mean a smaller size for each transistor. To keep pace with Moore’s law, various techniques (e.g. phase-shifting mask photolithography, electron beam lithography) have been developed to enable the fabrication of smaller transistors [4-6]. The state-of-the-art transistor is with 14nm gate manufactured by the Intel company, but the size of transistors cannot be infinitely scaled down. To maintain the electrically insulating property of the gating layer made of a silicon oxide film, its thickness has to be greater than four atomic layers [7,8]. This fundamental physical limit will be reached in the near future with the current speed of development in the semiconductor industry. In addition, the effect of defects may start to emerge with the shrinking size of transistors, which may lead to statistical errors in the binary data processing. Therefore, a new approach has to be explored to meet these technical challenges.
A promising alternative strategy is the bottom-up approach, where individual building blocks (e.g. atoms, molecules) are placed or self-assembled that the devices with the desired functions can be generated. The bottom-up approach is therefore considered a promising method to minimize the scale of nanodevices while offering unlimited possibilities for designing and fabricating nanodevices. In the bottom-up approach, two main methods have been developed to implement nanosystems with atomic precision: the manipulation method and the self-assembly method. In the manipulation method, individual atoms or molecules are manipulated by scanning probe microscopy to build nanostructures. In the self-assembly method, molecules automatically arrange themselves into an ordered structure.

The manipulation method came into being with the invention of scanning tunneling microscopy (STM) in the early 1980’s [9]. In 1983, Gerd Binnig and Heinrich Rohrer presented the atomically resolved real-space image of the 7×7 reconstructed surface of Si acquired with STM, which opened up the possibility to investigate surface phenomena at atomic scale [10]. Later, Eigler and Schweizer constructed a patterned array of xenon atoms representing the trademark of the IBM company on a Ni(110) surface by positioning xenon atoms with a STM tip. This showed that STM could serve not just as a tool for imaging surface phenomena but also as a powerful tool for constructing structures at atomic level [11]. In 1993, Eigler reported the famous “quantum corral” built with Fe atoms on a Cu(111) surface via the atom manipulation technique of STM, which showed the capability of locally modifying the electronic properties of a Cu(111) surface [12]. Since then, various nanostructures have been constructed via the manipulation method and interesting properties (e.g. the quantum confinement effect) of these nanostructures have been reported [13-17]. The direct manipulation of the building blocks enables researchers to control the construction process of
nanostructures with ultimate precision, but it is almost impossible for the researchers to arrange the extremely large amount of elementary building blocks within a reasonable amount of time. Although model structures can be constructed in the atom-by-atom fashion and characterized as a proof of concept, the extremely time-consuming process of the manipulation method hinders its further applications.

How to arrange trillions of elementary building blocks into an ordered structure in a short time? The self-assembly method offers a promising solution. Self-assembly is the autonomous process in which elementary building blocks assemble into an ordered structure via weak interactions [18]. Since no human intervention is needed during the assembling process, this method allows for the synthesis of ordered nanostructures in a relatively short time. In molecular self-assembly, molecules act as the elementary building blocks. The assembling process is dominated by noncovalent intermolecular bonding (e.g. hydrogen bonding, van der Waals force, halogen bonding, metal-ligand bonding). By tailoring the size, shape, symmetry and functional groups of the molecule, the assembling process can be controlled at the molecular level to enable the formation of molecular nanostructures with designed functionalities [19-23].

1.2 Thesis outline
In this thesis, we studied the two-dimensional molecular self-assemblies on metal and graphene surfaces by means of scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), low energy electron diffraction (LEED) and angle-resolved photoemission spectroscopy (ARPES). Our central goal was the controllable tuning of the electronic properties of metal surfaces and graphene by molecular patterning. To achieve this goal, we utilized molecules with different functional groups to form porous
network structures with long-range order. We performed STM and LEED measurements to gain the structural information of the molecular self-assemblies. STS and ARPES measurements were performed to investigate the influence of the molecular self-assemblies on the electronic properties of the underlying substrates. The thesis is organized as follows:

**Chapter 2** briefly reviews the up-to-date research work on the molecular self-assembly on surfaces. This chapter also discusses the non-covalent intermolecular interactions that govern the assembling processes on surfaces. A brief explanation on principle of quantum confinement effect is given. The idea of tuning the electronic properties of metal surfaces and graphene is also briefly introduced.

**Chapter 3** gives an overview of the experimental techniques used in this thesis. The working principle of STM is first described followed by a short introduction of STS. Then the theory of ARPES is presented, at last, the LEED technique is briefly explained.

**Chapter 4** reports a comparative study of the self-assemblies of 1,3,5-benzenetribenzoic acid (BTB) on graphene/Cu(111) and BTB on bare Cu(111) surface. STM measurements showed that the BTB molecules deposited on Cu(111) formed a close-packed pattern after annealing, while the BTB molecules deposited on graphene/Cu(111) formed a porous network after annealing. The drastic difference in molecular arrangements indicates that graphene can effectively decouple the molecules from the underlying substrate.

**Chapter 5** presents a study of the quantum dot array arising from the confinement effect of the hexagonal porous network formed by BTB molecules on Au(111) surface. STS and ARPES measurements demonstrate that the electronic properties of the Au(111) are modulated by the presence of
the porous network, which demonstrates that the electronic properties of metal surfaces can be tailored by molecular patterning.

**Chapter 6** reports the formation of a hexagonal porous network by the subsequent deposition of para-hexaphenyl-dicarbonitrile (NC-Ph$_6$-CN) molecules and Co atoms on Au(111) surface. Band folding and band gap opening of the surface state band of Au(111) are observed in the ARPES measurement, indicating that the electronic properties of the Au(111) are tuned by the molecular self-assembly on the macroscopic scale.

**Chapter 7** reports the formation of metal-coordinated molecular self-assemblies on graphene/Ir(111) surface by the subsequent deposition of NC-Ph$_6$-CN molecules and Cu atoms. By varying the stoichiometry between the NC-Ph$_6$-CN and the deposited Cu atoms, the molecules can form basketweave pattern, hexagonal porous network and molecular chain accordingly. The formation of the metal-coordination bonding is evidenced by the Cu atoms resolved in STM images. STS measurements demonstrate that the structural transformation modulates the electronic properties of NC-Ph$_6$-CN molecules and Cu atoms.
References


Introduction


