Tuning the electronic properties of metal surfaces and graphene by molecular patterning
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Conclusions and Perspectives

The controlled manipulation of matter on the microscopic scale to achieve tunable materials properties on the macroscopic scale is at the heart of nanoscience and -technology. Artificial nanostructures built by making use of the scanning tunneling microscopy (STM) manipulation method, e.g. quantum corrals, were shown to locally modify the electronic surface properties of metals by confining the surface state electrons. Though the STM manipulation method offers ultimate control and precision in building artificial nanostructures, it is impractical to be used for adjusting the properties of an entire macroscopic surface since it is very time consuming. On the other hand, via noncovalent intermolecular interactions well-ordered two-dimensional molecular porous networks can be created on surfaces. It has been reported that an artificial 2D dispersive electronic band structure can be formed on a Cu(111) surface after the formation of a nanoporous molecular network, which indicates that molecular self-assembly may serve as a promising way to tune the electronic properties of metal surfaces and perhaps even graphene on a macroscopic scale.

In this thesis, we synthesized well-ordered molecular porous networks on both graphene and metal surfaces. Ultra-high vacuum (UHV) low-temperature scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) measurements were performed to gain insight on the structure of the molecular networks. Scanning tunneling spectroscopy (STS) and angle-resolved photoemission spectroscopy (ARPES) measurements were performed to study the influence of the molecular network on the electronic properties of the underlying substrates.
In Chapter 3, a comparative study on the molecular self-assembly of 1,3,5-benzenetribenzoic acid (BTB) molecules on Cu(111) and graphene/Cu(111) is reported. On Cu(111), the BTB molecules were found to mainly arrange in close-packed structures stabilized by hydrogen bonding between the partially deprotonated carboxylic acid end groups. In addition, porous structures formed by intact BTB molecules were also observed, which are based on hydrogen bonding between the neighboring molecules. On graphene/Cu(111), the BTB molecules mainly formed porous structures accompanied by small patches of disordered close-packed structures. After annealing, the BTB molecules adsorbed on Cu(111) were fully deprotonated and arranged in the close-packed structure. In contrast, the porous network was exclusively formed on graphene/Cu(111) after annealing. The different structures formed by the BTB molecules on these two substrates indicate that the molecular self-assembly behavior is highly dependent on the first substrate layer. Though graphene is only a single layer of carbon atoms, it can effectively decouple the adsorbed molecules from the underlying metal substrates.

In chapter 4, a detailed study of the porous network formed by BTB molecules on Au(111) is reported. STM measurements showed that the molecules were arranged in a honeycomb lattice, similar to the ones observed on Cu(111) and graphene/Cu(111). The diffraction spots observed in the LEED image indicated the long-range order of the molecular network. STS measurements showed that the surface state electrons of Au(111) are confined in the cavities of the porous network, which resulted in the formation of a regular quantum dot array. Due to leaky confinement, the confined states can couple leading to the formation a new band structure which was observed in ARPES measurements. Our study shows that
molecular patterning can serve as a promising tool to macroscopically tune the electronic properties of metal surfaces in a controllable manner.

In chapter 5, a combined STM and ARPES study on the metal-coordinated hexagonal porous network formed by Co atoms and para-hexaphenyl-dicarbonitrile molecules (NC-Ph$_6$-CN) on Au(111) is presented. STS spectra showed that the surface state electrons of Au(111) were confined due to the potential induced by the porous network. A new band structure was observed in the ARPES measurements which demonstrate that the electronic properties of metal surfaces can be modified due to the periodic potential induced by the well-ordered porous network.

In chapter 6, the synthesis and characterization of metal-coordinated molecular self-assemblies from NC-PH$_6$-CN molecules and co-deposited Cu atoms on graphene/Ir(111) is presented. By tuning the stoichiometry between the deposited Cu atoms and the molecules, different kinds of molecular self-assemblies can be formed. For a 3:2 ratio, a two-dimensional hexagonal porous network based on three-fold Cu-coordination was observed while for a 1:1 ratio, one-dimensional molecular chains based on two-fold Cu-coordination were formed. The formation of the metal-coordination bonding was evidenced by clearly imaging the individual Cu atoms with STM. STS measurements demonstrated that the electronic properties of NC-Ph$_6$-CN molecules and Cu atoms are different for the two-dimensional porous network compared to the one-dimensional molecular chains.

In conclusion, we studied the molecular self-assemblies formed by the BTB and NC-Ph$_6$-CN molecules on graphene and metal surfaces by using STM, STS, LEED and ARPES measurements. Due to leaky confinement inherently present for molecular porous networks, the confined surface states can couple,
resulting in the formation of new band structure as observed in ARPES measurements. According to theoretical considerations, the electronic properties of graphene can be changed when an external periodic potential is applied onto it. In this sense, the molecular patterning method holds the promise of tuning the electronic properties of graphene due to the periodic potential induced by it. Therefore, it is beneficial to first study the molecular self-assembly formed on graphene. The different adsorption behavior of BTB molecules on Cu(111) and graphene/Cu(111) showed that graphene effectively decoupled the adsorbed molecules from the underlying metal substrate. By co-adsorption of NC-Ph$_6$-CN molecules and Cu atoms, 2D metal-organic coordination networks stabilized by metal-ligand interactions were synthesized on graphene/Ir(111). Our results show that the molecular patterning method enables the construction of well- and long-range-ordered 2D molecular arrangements on graphene whose potential for tailoring the electronic properties of metal surfaces and graphene can now be investigated in a next step.

As a perspective for future work, it would be beneficial to study molecular self-assembly on graphene with angle-resolved photoemission spectroscopy. In this way, the modification of the band structure of graphene due to the periodic potential induced by well-ordered porous networks can be directly observed. For commensurate molecular self-assemblies formed on graphene, an external potential can be imposed onto one of the two sublattices of graphene, which may lead to a band gap opening at the K point of the Brillouin zone of graphene.