

University of Groningen

Tailoring molecular nano-architectures on metallic surfaces

Solianykh, Leonid

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version

Publisher's PDF, also known as Version of record

Publication date:

2019

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Solianykh, L. (2019). *Tailoring molecular nano-architectures on metallic surfaces*. [Thesis fully internal (DIV), University of Groningen]. University of Groningen.

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Summary

In order to improve the performance of semiconductor electronic devices, miniaturization involving a higher level of structural complexity is required. This scaling down process is soon expected to face fundamental physical limits, for instance, insufficient electrical insulation, which will adversely affect the performance of the fabricated devices. Therefore, it is important to explore new approaches for fabricating (nano)electronic devices. A promising alternative approach is based on molecular self-assembly which is defined as the spontaneous association of well-defined molecular building blocks into ordered structures stabilized by non-covalent bonds. Ubiquitous in biological systems, molecular self-assembly can be used for building nanoscale functional systems which are envisaged to find their applications in (nano)electronic devices. On a surface, molecular self-assembly is governed by the subtle interplay between non-covalent, intermolecular and molecule-substrate interactions. By carefully designing the molecular building blocks, the interplay between the interactions can be tuned leading to the formation of complex organic nanostructures exhibiting versatile functional properties. The aim of the work in this thesis was to understand how we can create self-assembled nanostructures with desired functional properties in a controllable manner. Such an understanding is, among others, fundamental for applications in *organic* and *molecular* electronics. In this regard, we gained insight into the self-assembly of organic functional molecules on well-defined metal surfaces by means of scanning tunnelling microscopy (STM) and spectroscopy (STS), low-energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS) as well as normal incidence X-ray standing wave (NIXSW) and near-edge X-ray absorption fine structure (NEXAFS) measurements.

In *Chapter 3*, the self-assembly of pyridyl-functionalized triarylamine molecule **1** on Au(111) is studied with STM, LEED, XPS and NEXAFS. The STM and LEED data showed that the molecules can arrange into three long-range ordered phases stabilized by different non-covalent interactions. One of the phases is held together by hydrogen bonding, while the other two phases are stabilized by metal-ligand interactions between the molecules and Au atoms, which originate from the underlying substrate. The two metal-coordinated phases exhibit Au-coordination with two- and three-fold symmetry. Which of the observed structures is present on the surface, can be controlled *via* the substrate temperature. For instance, deposition of submonolayer coverage of molecule **1** onto the substrate kept at room temperature

resulted in the coexistence of all three phases. In contrast, annealing at 180 °C promoted the formation of the phase stabilized by two-fold metal-coordination, which was identified as the phase with highest thermal stability. We suggest that the three-fold coordinated phase is kinetically trapped, while the two-fold coordinated one represents thermodynamic equilibrium. This can be rationalized by the fact that elevated sample temperatures are required for generating enough Au adatoms that only the two-fold coordinated phase forms. In addition, the XPS and NEXAFS data showed that the chemical environment as well as conformation of the molecules is different for the hydrogen-bonded phase compared to the two-fold metal-coordinated phase. According to our XPS analysis, the binding energies of the C 1s and N 1s core levels of the molecules increase when the molecules undergo two-fold Au-coordination. For the N 1s core level of pyridylic nitrogen atoms which are directly involved in the metal-coordination, the binding energy increases the most, around +0.7 eV, while for the C 1s and N 1s core levels of other atoms, the binding energy increases less, around +0.3 eV. Our NEXAFS analysis showed that the core of molecule **1** flattens, while the pyridyl functional groups bend more towards the surface for the two-fold metal-coordinated phase compared to the hydrogen-bonded one.

For future work, it would be interesting to study the self-assembly of molecule **1** on Au(111) by means of NIXSW measurements. In this way, the adsorption distances of the comprising molecular moieties to the underlying surface can be obtained. The aforementioned distances will give deeper insight into the conformation of the molecules as well as into the strengths of the related molecule-substrate interactions. In addition, a STS study of the observed molecular phases on Au(111) will shed light onto the electronic properties of the surface patterned by organic molecules. Finally, it will be interesting to fill the observed porous phases with guest molecules and study the resulting surface electronic properties.

In *Chapter 4*, a combined STM and STS study of the self-assembly of pyridyl-functionalized triarylamine molecule **2** on Au(111) is described. The STM measurements showed that two porous molecular structures coexist on the surface after submonolayer deposition at room temperature. The short-range ordered structure is held together by a combination of hydrogen bonding and Au-coordination with two-fold symmetry while the long-range ordered two-dimensional phase is exclusively stabilized by Au-coordination with three-fold symmetry. After annealing at 120 °C, the long-range ordered phase with three-fold Au-coordination remains on the surface, while the short-range ordered phase disappears and a new long-range ordered phase exclusively stabilized by metal-ligand interactions with two-fold symmetry emerges. We concluded that the stabilization energies for the two long-range ordered Au-coordinated phases are similar. In addition, the observed self-assembly was compared to the one of molecule **1**. We noticed that the formation of similar structures with two-fold coordination became possible at different substrate

temperatures, for molecule **1** at room temperature and for molecule **2** at 120 °C. This difference is related to the structural differences of the two molecules, which results in different molecule-substrate interactions. In addition, when studying the electronic properties of the Au(111) surface covered with the two-fold Au-coordinated phase by STS, we found that the aforementioned porous structure can confine the surface state electrons inside its pores.

Subsequent studies are suggested for characterizing the observed confinement in detail and to conduct a similar STS study for the molecular structure with three-fold coordination. In this way, the surface electronic properties of the Au-coordinated porous structures exhibiting different pore sizes can be compared, which is of practical interest for building organic-based electronic devices.

In *Chapter 5* we showed how the electronic properties of Au(111) can be tuned by molecular patterning in a controllable manner. By using cyano-functionalized molecular linker and Co atoms, we created a metal-coordinated porous network on the Au(111) surface and investigated its surface electronic properties with STM, STS and ARPES. The STM and STS data indicate that the aforementioned long-range ordered porous network partially confined the surface state electrons inside its pores. Such imperfect electron confinement allows coupling between neighbouring confined states, leading to the formation of a new electronic band structure which was confirmed by ARPES measurements. Our study demonstrates that molecular patterning is a promising tool for controllable tuning of the surface electronic properties of metals on a macroscopic scale.

For future experiments, one can think of filling the pores of the metal-organic network with guest molecules or metal atoms to find out how the electron confinement is affected by guest species and whether there is a correlation between the adsorption behaviour of guest species and the electron distribution inside the pores.

In *Chapter 6*, we illustrated our combined XPS and NIXSW study on the conformation and molecule-substrate interactions of the pyridyl-functionalized free-base porphyrin molecules in a close-packed arrangement on Ag(111). We determined the binding energies of the C 1s and N 1s core levels as well as the adsorption heights for the chemically different atomic species within the molecules. We concluded that the molecule-substrate interaction is of chemisorptive character. The porphyrin molecules mainly interact with the Ag surface via their nitrogen atoms of the pyridylic end groups, while the porphyrin macrocycles interact less and the pentyl chains remain further away from the surface. The mentioned molecule-substrate interaction results in a molecular conformation with a large difference in maximum and minimum adsorption heights of 0.86 Å, for the closest pyridylic nitrogen atoms and furthest pentyl chain carbon atoms with respect to the underlying Ag(111) surface.

For future work, it will be interesting to metalate the macrocycle of studied porphyrin molecules with magnetic metal atoms such as Co or Fe and study their chemical environment and conformation on Ag(111) with XPS and NIXSW. Such a study will give insight on how magnetic metal atoms affect molecule-substrate interactions and conformation of the molecules, paving the path towards applications of metalated porphyrin molecules as single-molecule magnets.