Tuning the electronic properties of metal surfaces and graphene by molecular patterning
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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2018

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Li, J. (2018). Tuning the electronic properties of metal surfaces and graphene by molecular patterning. [Groningen]: University of Groningen.

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Chapter 5

A porous molecular network on Au(111): confining the surface state as well as the surface potential of the reconstructed surface

A self-assembled nanoporous network with long-range order is formed by 1,3,5-benzene tribenzoic acid molecules on Au(111). By utilizing scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), angle-resolved photoemission spectroscopy (ARPES) and boundary element method (BEM) calculation, we reveal that the electronic structure of the Au(111) surface is changed due to the periodic potential induced by the molecular network. The lateral confinement of the surface state electrons in the pores of the molecular network leads to the formation of a regular quantum dot array. Due to leaky confinement, the confined states can couple and a 2D band structure is formed. Moreover, the interplay of the periodic potential introduced by the adsorption of the porous molecular network with the varying surface potential of the face-centered-cubic (fcc) and hexagonal-close-packed (hcp) areas of the Au(111) surface results in an additional variation of the surface state band structure; i.e. a gap is introduced into the artificial 2D band structure. 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.
5.1 Introduction

The controlled manipulation of matter on the microscopic scale to achieve tunable macroscopic materials’ properties is at the heart of nanoscience and technology. Artificial nanostructures built through the scanning tunneling microscopy (STM) manipulation method, e.g. quantum corrals, were shown to modify the electronic surface properties of metals locally by confining the surface state electrons [1-5]. Though the STM manipulation method offers ultimate precision in building artificial nanostructures, it is impractical to be used for adjusting the properties of an entire macroscopic surface since it simply is too time-consuming. On the other hand, band folding and band gap opening of surface state bands have been observed on vicinal metal surfaces suggesting that the electronic properties of entire metal surfaces can be tuned by the periodic potential exerted by the vicinal surface [6-12]. Since the main adjustable parameter of this method is the terrace width, only a very limited amount of control can be exercised. A further possibility is molecular self-assembly which offers the possibility to build up large-area, well-ordered nanostructures on surfaces in a short amount of time. As a parallel process, the molecules quickly arrange themselves into an ordered structure via non-covalent intermolecular interactions and without human intervention [13,14]. In this way, a periodic scattering potential for surface state electrons can be formed on a metal surface in the form of porous networks, allowing the controlled modification of the surface state band structure. By using molecular building blocks with different sizes and geometries, the pore size as well as the symmetry of the porous networks can be adjusted, which allows for tuning the electronic structure of the whole surface in a controllable way. Lobo-Checa et al. were the first to show the formation of a quantum dot array on Cu(111) by molecular self-assembly of a perylene derivative, which enabled the surface state confinement in the network pores,
resulting in a new dispersive band due to the coupling of neighboring quantum dots [15, 16]. For a family of linear linker molecules, Co-coordinated porous molecular networks having similar geometries but different sizes were built up on Ag(111), which allowed for a tunable energy level alignment [17, 18]. The surface state band bottom of Cu(111) was reported to be shifted towards the Fermi level due to the potential induced by the porous network built with 9,10-dicyanoanthracene molecules [19]. The confined surface state electrons in the pores of the molecular network were observed to influence the adsorption behavior of the deposited atoms [20, 21]. In this study, we synthesized a porous molecular network by depositing 1,3,5-benzenetribenzoic acid (BTB) on Au(111). This gives us the possibility to study the interplay between the inherent surface potential associated with the reconstructed surface of Au(111) and the periodic potential induced by the molecular network. STM measurements showed that the molecules were arranged in a honeycomb lattice due to intermolecular hydrogen bonding between the carboxylic acid groups. The diffraction pattern observed in low-energy electron diffraction (LEED) measurements indicated long-range order of the molecular network. Scanning tunneling spectroscopy (STS) measurements showed that the surface state electrons on Au(111) were restricted to discrete energy levels due to quantum confinement effect in the cavity of the network. Band gap opening in the surface state band of Au(111) was observed in the ARPES measurement. The experimental data and the boundary element method (BEM) calculation indicate that the electronic properties of the surface state electrons are modulated by the surface potential induced by the porous network and the reconstructed surface.

5.2 Experimental results and discussion
The employed BTB molecule (Figure 5.1a) has a three-fold symmetric shape with three terminal carboxylic acid functionalities. Upon deposition of BTB on Au(111) and subsequent annealing at 400 K for 30 minutes, a well-ordered hexagonal porous network formed (Figure 5.1c) exhibiting domain sizes of 200 nm and more, only depending on the Au terrace sizes. The long-range order of the porous network was confirmed by LEED (see Figure 5.1d and Figure 5.1e). The LEED diffraction pattern showed that the porous network possessed an relative rotation of ± 3.5° with respect to the principal direction of the Au(111) substrate. From the detailed STM image (Figure 5.1b) with intramolecular resolution it can be clearly seen that the molecules are arranged in a honeycomb lattice. Each hexagonal pore consists of six molecules. The rhombic unit cell (indicated in blue in Figure 5.1b) has a size of a=b=3.28±0.14nm and an angle of Θ=60±0.5°. The proposed molecular model of the porous network is superimposed onto the STM image in Figure 5.1b. The molecules are lying flat on the Au(111) surface and each molecule undergoes double H-bonding with three neighboring molecules via the carboxylic endgroups. The intermolecular double hydrogen-bonds between adjacent molecules is the main driving force for the formation of the long-range ordered network while the molecule substrate interactions are assumed to be relatively weak since the intact herringbone reconstruction is visible through the molecular overlayer (Figure 5.1c). In general, the formation of the porous molecular network is similar to what has been observed on Ag(111) [23], graphite [24] and graphene [25].
A porous molecular network on Au(111): confining the surface state as well as the surface potential of the reconstructed surface

Figure 5.1. (a) Structure of 1,3,5-benzentribenzoic acid (BTB). Gray: carbon atoms, red: oxygen atoms, white: hydrogen atoms. (b) Detailed STM image (8.4 nm × 8.4 nm) of the honeycomb network. The unit cell is marked in blue. The proposed molecular model for the BTB honeycomb network is overlaid onto the STM image. (c) After annealing at 400 K, the BTB molecules exclusively arrange in a
honeycomb network as can be seen from this large-scale overview STM image (200 nm × 100 nm). (d) LEED image for the BTB network on Au(111) after annealing taken at 103 eV. The (0,0) and first order spots of the Au(111) surface are visible. (e) LEED image for the BTB network on Au(111) after annealing taken at 14 eV. Spots originating from the porous BTB network are visible.

Figure 5.2. (a) STS spectra taken on the fcc (black) and hcp (blue) zone of the bare Au(111) substrate. (b) STS spectra taken in the center of a bright pore located on a hcp area (blue line, position marked in (d) by a blue dot) and a dark pore located on a fcc area (black line, position marked in (d) by a black dot). (c) Topography image for submonolayer coverage of BTB on Au(111) after annealing at 400 K (30 nm × 30 nm). (d), (e) dI/dV maps acquired simultaneously with the STM image displayed in (c) at -0.40 V and -0.25 V, respectively (30 nm × 30 nm).
To investigate the influence of the porous BTB network on the electronic surface properties of Au(111), STS measurements were performed in an area where both the bare Au(111) surface and the porous network were present (Figure 5.2c). The STS spectra acquired in the fcc and the hcp zone, respectively, of the bare Au(111) surface are displayed in Figure 5.2a and serve as a reference for the measurements performed in the areas covered by the BTB network. Clear differences are present between these two curves: the STS spectrum taken in the hcp zone exhibits an almost $\delta$-like increase directly at the surface state onset, while the STS spectrum taken at the fcc zone shows the same $\delta$-like increase directly at the surface state onset but with a considerably decreased amplitude. The STS spectrum of the hcp zone reaches its peak value at -0.48 eV, the STS spectrum of the fcc zone reaches its peak value at -0.42 eV. According to previous studies, this behavior was caused the periodically varying potential of the Au(111) herringbone reconstruction [26-29], which can be quantitatively explained by the Kronig-Penney model [26]. In analogy to previous works, which reported surface state confinement in molecular pores adsorbed on metal surfaces having a surface state [15-21], the potential induced by the BTB network can be expected to lead to confinement of the Au surface state electrons inside the pores. The eigenenergies of the confined states can then be approximated by using the particle in a box model, consequently rendering each pore a quantum dot. When performing STS measurements inside a pore, three cases have to be differentiated. The pore is either located on a hcp or fcc area or on both a hcp and fcc area. In the following, we will only consider the two extreme cases (pore on either hcp or fcc area) since the third case is a mixture of the former two. The STS spectra acquired in the center of the two kinds of pores are shown in Figure 5.2b. While for the pore on the hcp area the entire region between -0.42 V and -0.25 V shows high intensity and individual
A porous molecular network on Au(111): confining the surface state as well as the surface potential of the reconstructed surface

peaks are not easily discernible, for the pore on the fcc area two peaks located around -0.36 V and -0.25 V can be identified. To examine the spatial distribution of the local density of states (LDOS), dI/dV maps were acquired at energies of -0.4 eV (Figure 5.2d) and -0.25 eV (Figure 5.2e). For surface state confinement in the pores, a high intensity of the LDOS signal has to then be present in the pores. However, for -0.4 eV only a striped pattern both on the bare Au surface and on the area covered by the molecular network was observed. From that we conclude that at this energy no surface state confinement in the pores of the molecular network takes place. On the other hand, at -0.25 eV dome-like features were observed in the center of the pores, which is a typical sign for quantum confinement. In the following, we will first continue discussing the surface state confinement before looking into the underlying reason for the appearance of the striped pattern at -0.4 eV.

**Figure 5.3.** Confinement of the surface state electrons of Au(111) by the BTB network. (a) STM image (4 nm x 4 nm) of an individual BTB pore. (b), (c) and (d) Experimentally acquired dI/dV maps taken at -0.25 V, -0.1 V and 0.25 V. (e) STS spectrum taken at the center position (red curve, position marked by the red square in Figure 5.3a) and STS spectrum taken at the halfway position (green curve, position marked by the green square in Figure 5.3a). (f), (g) and (h) The LDOS at -
A porous molecular network on Au(111): confining the surface state as well as the surface potential of the reconstructed surface

0.25 V, -0.1 V and 0.25 V calculated by the boundary element method (BEM). The molecules are represented by the hexagons arranged in the triangular shape.

To further examine the confinement of the Au surface state in the pores of the BTB network, we focused on a pore located on a hcp zone of the Au(111) surface (Figure 5.3a). For STS measurements taken at the center as well as at halfway between the center and the pore edge (see Figure 5.3e), local maxima (besides the one at -0.4 eV) were observed at energies of -0.25 eV (center position), -0.1 eV (halfway position) and +0.25 eV (center position).

To study the spatial distribution of the LDOS, dI/dV maps were taken at these three energies. The dI/dV map taken at -0.25 eV (Figure 5.3b) exhibits a dome-like shape with the highest intensity in the center of the pore, which corresponds to the ground state energy of the first confined state. The dI/dV map taken at -0.1 eV (Figure 5.3c) has a donut shape with the highest intensity located between the pore center and its rim and shows the spatial distribution of the second eigenstate. The dI/dV map taken at +0.25 eV shows a more complicated structure than the previous two patterns. In addition to the central maximum, six maxima close to the positions of the molecules were observed. This pattern represents the spatial distribution of the third eigenstate. To gain further insight into the confinement effect induced by the porous network, we calculated the LDOS inside the cavity at the energy of -0.25 eV, -0.1 eV and +0.25 eV with BEM calculation (see figure 5.3f, 5.3g and 5.3h) [30, 31]. The BEM is developed by García de Abajo which has been extensively used for solving Maxwell’s equations and optical response for arbitrary shapes. This method is suitable for studying the regions with constant potential, while the boundaries between regions with abrupt potential change. In the calculation, the molecules are assigned a potential of 0.47 eV while the Au surface is assigned a potential of 0 eV. The features
observed in the experimental acquired dI/dV map in Figure 5.3 can be quantitatively reproduced in our calculated result. The nice match between the experimental data and the calculation supports our interpretation on the features observed in the dI/dV map. The STS and dI/dV maps indicate that the molecular network formed by BTB molecules can function as a potential barrier to confine the surface state electrons of the Au(111) surface. The confinement effect restricts the surface state electrons to discrete energy levels in the cavity of the molecular network. Therefore, each pore can be considered as a quantum dot, and a regular quantum dot array is generated due to the inherent periodicity of the molecular network.

Figure 5.4. (a) STM image (7.6 nm x 7.3 nm) of the porous network taken simultaneously with the dI/dV maps (b), (c) dI/dV maps taken at -0.4 eV and -0.25 eV, respectively. (d) Schematic of the potential landscape of the BTB network on Au(111) used for the BEM calculations (e), (f) Spatial distributions of the LDOS at -0.4 eV and -0.25 eV, respectively, calculated with the BEM method.
Now, we will focus on the stripe pattern observed in the dI/dV map taken at -0.4 eV. Comparing Figures 5.2c and 5.2d reveals that the dark stripes locate on fcc zones while the bright stripes locate on the hcp zones and the corrugation lines. This observation indicates that the stripe pattern obtained at -0.4 eV has a close relationship with the herringbone reconstruction of Au(111). It has been reported that the dI/dV map acquired on bare Au(111) at -0.48 eV also exhibits stripped pattern due to the different intensity of LDOS in the fcc zone and hcp zone of the reconstructed surface [26, 28]. According to the previous study, the different packing density of Au atoms between the fcc and hcp region gave rise to a superlattice with periodically varying potentials, which resulted in the spatial and energetic rearrangement of the surface state electrons of Au(111) [26]. In response to this potential superlattice, the surface state electrons with lower energy tend to be localized in the hcp region of the reconstructed Au(111) surface, while the trend is reversed for the electrons with relatively higher energy, shifting the LDOS to the fcc region to the reconstructed Au(111) surface. In analogy to the previous study, here, we propose that the spatial and energetic distribution of the surface state electrons of Au(111) are modulated by the potential superlattice induced by the reconstruction and the porous network. Due to the leaky confinement effect induced by the pure organic molecular network, a coupled quantum dot array is formed, which results in the formation of an artificial two-dimensional dispersive band structure observed around -0.4 eV. In the meantime, the spatial and energetic distribution of the surface state electrons are also influenced by the potential superlattice induced by the reconstructions. As a result, the low energy surface state electrons tend to be localized in the hcp region while the electrons with relatively higher energy are shifted to the fcc region, which lead to the stripe pattern observed in the dI/dV map at -0.4 eV.
To gain insight into the underlying mechanism of the stripe pattern, we calculated the local density of states at the metal-organic interface with the BEM calculation [30, 31]. The potential landscape for the calculation is shown in figure 5.4d. The potential difference between the fcc and hcp region has been estimated to be 25 meV in previous studies. [26, 27]. Therefore, we assign a potential of -25 meV for the hcp zone and a potential of 0 meV for the fcc zone and the hydrogen bonding point. For the BTB porous network, we assign a potential of 310 meV. The band onset of the surface state band is determined to be -0.48 eV from the STS data, and the effective mass is 0.27 m_e, which is in agreement with previous studies [26, 27, 32, 33]. Figure 5.4e shows the calculated LDOS at -0.4 eV, the fcc zone appear relatively darker, which corresponds to a lower LDOS, while the hcp zone appears brighter which corresponds to the higher LDOS. The stripe pattern with alternating brightness is nicely reproduced by our calculation. Compared to the experimental data in Figure 5.4b, a good agreement between the calculated data and the experimental results is reached, which support our interpretation that the electronic properties of the Au(111) substrate are influenced by the surface potential induced by the porous network and the herringbone reconstruction. To check the spatial distribution of the surface state electrons at higher energy, the LDOS is also calculated at -0.25 eV (see Figure 5.4f). In this case, the fcc zone is with a higher LDOS while the hcp zone is with a lower LDOS, which shows an inverse in brightness compared the LDOS at the -0.4 eV. Figure 4c shows the dI/dV map taken at the -0.25 eV, the intensity of fcc zone is indeed higher than that of the hcp zone at -0.25 eV. The calculated data shows a good consistence with the experimental results for both low energy and high energy electrons, which further support our interpretation that the electronic properties of the Au(111) are modulated by the potential superlattice induced by the molecular network and the
A porous molecular network on Au(111): confining the surface state as well as the surface potential of the reconstructed surface

reconstructions.

Figure 5.5. ARPES measurements for the porous BTB network on Au(111) taken along the ΓM (a) and ΓK direction (b), the second derivative of the energy dispersion curves are taken to enhance the gap openings (c), (d) Simulated energy dispersion curves based on the BEM calculations.

It has been reported that the coupled quantum dot array can give rise to the formation of a new dispersive band structure[15, 16], and the periodic potential superlattice can lead to the band gap opening at the Brillouin zone boundary as indicated by the Kronig–Penney model [7, 11, 34-38]. In view of this, ARPES measurements were performed at 150K to study the band structure of the Au(111) surface with the porous network on it. Figure 5.5a and Figure 5.5b show the second derivative of the ARPES data of porous network on Au(111) plotted along the ΓM direction and the ΓK direction. As shown in the image, a new dispersive band is formed due to the coupling of the neighboring quantum dots induced by the leaky confinement effect. The
band bottom is observed around -0.4 eV, which is in agreement with the STS data shown in Figure 5.2b. It is notable that the dispersion of the new band is relatively broad compared to the results reported in the previous study[15]. The LEED diffraction pattern has shown that the molecular network formed on Au(111) has two mirror domains with an relative rotation of ± 3.5° with respect to the principal direction of the Au(111) substrate. Therefore, the porous network leads to the formation of quantum dot arrays aligned in two directions with a relative angle of 7°, which results in the formation of two sets of new band structures with a relative rotation of 7° in the reciprocal space. When ARPES data is plotted along high symmetry points of one set of the new band structure, it also has contributions from the other set of the new band structure. Therefore, the dispersion of the electrons appears to be broadened due to the relative rotation between these two sets of new band structure. Another notable feature in the ARPES image is the dramatic decrease of the intensity observed around a certain momentum values. According to the Kronig–Penney model, band gap opening is expected at the Brillouin zone boundary due to the periodic potential imposed onto free electron system [7, 11, 34-38]. In our study, the band gap opening is observed around 0.11 Å⁻¹ along the ΓM direction and 0.13 Å⁻¹ along the ΓK direction, which corresponds the Brillouin zone boundary of the BTB porous network. Therefore, we assign the band gap opening observed in the ARPES data to the periodic potential induced by the molecular network. The band structure of the Au(111) surface with the BTB network is also calculated with the BEM method. As shown in figure 5.5c and 5.5d, the calculated image can quantitatively reproduce the features observed in the experimental data. Band gap opening is shown around the same momentum value and energy value, which further support our interpretation of the band gap in terms of the periodic potential induced by the porous network.
5.3 Summary and conclusion
To summarize, long-range ordered BTB porous network is synthesized on Au(111). The surface state electrons of Au(111) are confined in the cavities of the porous network, which leads to the formation of a coupled quantum dot array. A new dispersive band structure is formed due to the coupling of the neighboring quantum dots. The surface state band structure are changed due to the inherent surface potential associated with the reconstructed surface of Au(111) and the periodic potential induced by the molecular network. Our study shows that molecular patterning can serve as a promising tool to macroscopically tune the electronic properties of metal surface in a controllable manner.

5.4 Experimental methods
The STM measurements were performed in a two-chamber ultrahigh vacuum (UHV) system (base pressure ~ 10^{-11} mbar) with a low temperature STM (Omicron Nanotechnology GmbH) operated at 4.5 K. The STS measurements were performed at 4.5 K using a lock-in amplifier with a modulation amplitude of 10 mV (rms) and frequency of 678 Hz. The STM images were analyzed with the WSxM software [22]. The given bias voltages refer to a grounded tip.

The ARPES measurements were performed in a second UHV system (base pressure of 1*10^{-10} mbar) with a display-type hemispherical electron analyzer (SPECS Phoibos 150), an energy/angle resolution of 40 meV/0.1° and a monochromatized Helium I (hv= 21.2 eV) source. The sample temperature during measurements was 150K.

A clean and flat Au(111) substrate was prepared by repeated cycles of Ar+ sputtering and subsequent annealing at 700 K. BTB molecules were in situ
A porous molecular network on Au(111): confining the surface state as well as the surface potential of the reconstructed surface

sublimed from a Knudsen cell (540 K) onto the Au(111) substrate held at room temperature.

The boundary element method (BEM) is based on Green’s functions for finite geometries and electron plane wave expansion for periodic systems. To calculate the band structure, the particle-in-a-box model is extended to infinite 2D systems by defining an elementary cell and using periodic boundary conditions.
A porous molecular network on Au(111): confining the surface state as well as the surface potential of the reconstructed surface

References


A porous molecular network on Au(111): confining the surface state as well as the surface potential of the reconstructed surface


A porous molecular network on Au(111): confining the surface state as well as the surface potential of the reconstructed surface


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