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Self-Defined Transition State in Hybrid C₇₀-Au Clusters Created by the Scanning Tunnelling Microscope Tip

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Abstract: Manipulation of C₇₀-Au hybrid nanoclusters was investigated using a scanning tunneling microscope (STM) tip. We demonstrate that removing a selected C₇₀ molecule from the cluster by STM-tip resulted in an intermediate transition state without thermal decomposition. The molecule rotates and diffuses around the cluster and leaves the cluster without taking an additional molecule and Au atoms due to the rather weak interaction between molecules and the surface atoms. After removing C₇₀ molecule, the van der Waals interaction among C₇₀ molecules squeeze the cluster components and move out the Au atoms in the island. This self-transition-state is due to a weak charge transfer between the molecules and the surface. The extraction of the molecules in a ring cluster resulted in polygonal Au island formation in a major surface direction of Au(111). This preferential state for Au atoms after manipulation is staying on the surface because of a strong charge transfer with the surface atoms and thermal energy of the surface rather than C₇₀ molecules.

Introduction

When the physical dimensions of materials are reduced to the nanometer scale, new electronic, optical, or chemical properties can emerge [1]. Controlling the structure and fine tuning the properties of nanoscale materials require precise techniques [2]. Scanning probe microscopes (SPM), such as the scanning tunneling microscope (STM) and the atomic force microscope (AFM), are a family of versatile tools not only for atomic scale imaging, but also for material processing via atom manipulation [3-14]. Although these techniques are relatively slow and often needing cryogenic temperatures, recent scan speed improvement and multi-tip configurations significantly increase the speed of manipulation. The manipulations in the scanning tunneling microscope (STM) can be performed in many modes depending what is the fundamental force involved in manipulation as well as how atoms are transferred. Manipulation of atoms, molecules, clusters or nanoparticles by STM is always in direct competition with thermal processes and for this reason manipulation is usually performed at cryogenic temperatures. It is not straight forward to separate cleanly thermally excited processes from STM manipulation.

When atoms/molecules are deposited on solid surfaces, a number of events can occur including diffusion, nucleation, and island growth. These events depend on the surface temperature, structure, and adsorbate coverage. Under suitable conditions, magic number clusters can form [15, 16] via atomic close-packing, charge transfer, or van der Waals interactions [1, 17-20]. The investigation and manipulation of $(C_{70})_m-Au_n$ magic number clusters on the Au(111) surface have been extensively studied in our lab [7, 8, 18]. For the $(C_{70})_m-Au_n$ magic number cluster, only certain number of Au atoms (n) and C_{60} molecules (m) are allowed in the stable cluster. The cohesive energy of the $(C_{70})_m-Au_n$ cluster derives mainly from the charge transfer from gold to the C_{70} molecule and the van der Waals interaction among the C_{70} molecules. There is also the contribution of metallic bonding between Au atoms. In previous investigations, we modified $(C_{60})_m-Au_n$ clusters using the STM tip at both RT [8] and 110 K [7]. We were able to downsize the cluster using cascade manipulation in a controlled manner at RT. Here, we extend our study to the $(C_{70})_m-Au_n$ clusters that have been successfully fabricated on Au(111) [21]. We manipulated the $(C_{70})_m-Au_n$ cluster using the STM tip at RT and found metastable transition states for the cluster.

Experimental Methods

We use a (111) oriented gold film as the sample which is prepared in a BOC Edward 306 evaporator with a base pressure of 10^{-7} mbar via depositing Au onto preheated highly oriented pyrolytic graphite (HOPG) substrate at 493 K. The thickness of the Au film is estimated to be ~ 300 nm using a quartz-crystal thickness monitor close to the sample holder. The Au film is then transferred into an ultra-high vacuum (UHV) Omicron VT-STM chamber and Ar^+ ion bombardment and thermal annealing, up to 1000 K, cycles are performed to provide a large flat herringbone reconstructed Au(111) surface. An electrochemically etched W tip is used for imaging and manipulation of $(\text{C}_{70})_m\text{-(Au)}_n$ clusters after annealing *in-situ* up to 550 K. Hybrid $(\text{C}_{70})_m\text{-(Au)}_n$ clusters are produced via simultaneous deposition of 0.04 monolayer (ML) of C_{70} molecules and ~ 0.04 ML of Au atoms onto the Au(111) surface which is kept at 110 K. At this temperature, both the C_{70} molecules and the Au atoms diffuse on the surface and terminate either at the step edges or form irregular C_{70} -Au mixture at the elbow sites on the herringbone reconstructed Au(111) surface. Upon annealing to room temperature, the irregular C_{70} -Au mixture transforms into the hybrid $(\text{C}_{70})_m\text{-(Au)}_n$ clusters at the elbow site. Manipulation is conducted at RT.

Results and Discussion

All manipulation experiments were performed as follows [7, 8]. First, a selected area with cluster or island is scanned with -1.8 V sample bias voltage and 50 pA tunneling current. These tunnelling parameters are used for passive scanning because they do not cause any changes to the sample [22]. Then the STM tip is located above a preselected C_{70} molecule and driven towards the molecule for 1.25 nm over 12.8 ms which results in a mechanical interaction between the tip and the target molecule. The tip is then withdrawn to its initial height. During manipulation, the tunneling current is recorded as a function of the tip-surface distance for each experiment. After the manipulation event, we scan the area in order to find if the manipulation is successful or not. Figure 1 shows the extraction of a single C_{70} molecule from a compact C_{70} island. The successful manipulation accomplished at the tip-sample distance of 1.25 nm which is quite similar to the manipulation of the C_{60} molecule in a C_{60} -Au cluster [7, 8]. Figure 1 (A) is an STM image acquired just before the manipulation events and a single molecular vacancy can be seen in the middle of the molecular patch. In Figure 1 (B), the green dots indicate the locations where manipulation is performed. Two separate manipulation events, M1 and M2, take place. After each manipulation, the tip resumes to its normal scanning mode. Two new vacancies are created. The

one created by M1 stays in the location where it is created. The one created by M2 quickly diffuses away to the left edge of the C_{70} island. The pre-existing vacancy has also moved, Figure 1 (C).

There are two possible orientations of the C_{70} molecule on the Au(111) surface due to its unique rugby ball shape: the molecule can have its long or short molecular axis perpendicular to the substrate. At RT, the C_{70} molecules are able to rotate around both the long and short axis in the close-packed C_{70} layer at [23]. Therefore, the molecule does not take a fixed orientation at RT. The C_{70} island has well-defined edges parallel to the principal crystallographic directions of the Au(111) surface, such as $[11\bar{2}]$, $[01\bar{1}]$, and $[1\bar{1}0]$ directions [24].

Figure 1: Manipulation of individual C_{70} molecules in a C_{70} island. A. Before manipulation. B. During manipulation images on selected points (green dots). C. After manipulation image shows the created and recovered C_{70} vacancy on the island.

Manipulation experiments conducted on the close-packed C_{70} layers allow us to find the optimal operating conditions. For example, the probability of successfully extracting a C_{70} molecule depends strongly on the distance the tip travels towards the molecule. Once we have identified the optimal operating conditions, we begin to manipulate $(C_{70})_m-(Au)_n$ clusters. Similar to the formation of $(C_{60})_m-(Au)_n$ clusters [18], we find the following magic number clusters with C_{70} : $(C_{70})_7-(Au)_{19}$, $(C_{70})_{10}-(Au)_{35}$, $(C_{70})_{12}-(Au)_{49}$, $(C_{70})_{13}-(Au)_{51}$, $(C_{70})_{14}-(Au)_{63}$. Figure 2 shows the manipulation of a $(C_{70})_7-(Au)_{19}$ cluster. The C_{70} molecule in the middle of the cluster sits on a 2D hexagonal Au_{19} island. Therefore, orange and bright orange colors in the images represent lower and higher positions of C_{70} molecules. The three STM images are acquired before (A), during (B), and after (C) the manipulation which is performed at the location marked by a green dot in Figure 2 (B). The manipulation has

extracted a single C_{70} molecule from the cluster. The remaining six molecules stay together. We do not know if Au atoms have left the cluster or how many have left. Since there is still a raised C_{70} molecule, we came to the conclusion that most of Au atoms remain part of the cluster. In Figure 2 (C), we use the notation $(C_{70})_6-(Au)_{19}$ to show that there are six molecules left, although the number of Au atoms may be rather different from 19. The illustration of the cluster schematics are presented with before, during and after model in Figure 2 (D, E, and F), respectively. The schematic images show the cluster configuration with a ball model where the yellow balls show the Au island which is surrounded 6 C_{70} molecules and one on top of it and blue balls are the surface adatoms.

Figure 2: STM images demonstrate a single C_{70} manipulation by the driving STM tip in the hybrid $(C_{70})_7-(Au)_{19}$ cluster at room temperature. A, B and C are before, during, and after manipulation images, respectively. B. The manipulation performed on a selected C_{70} molecule indicated with a green dot. C. $(C_{70})_6-(Au)_{19}$ cluster obtained after manipulation. D, E, and F are the schematics diagram of the cluster and the manipulation processes with before, during and after manipulation, respectively. Yellow and blue balls represent Au island and the surface adatoms, respectively.

Figure 3 shows a series of STM images before and after the manipulation on a $(C_{70})_{13}-(Au)_{51}$ cluster. The $(C_{70})_{13}-(Au)_{51}$ cluster shown in Figure 3(C) has three raised (bright) C_{70} molecules. Each of the raised molecule sits on a hexagonal Au island. There are three edge-sharing Au islands in a row with a total number of 51 Au atoms. The manipulation performed by positioning the tip above the center molecule (indicated with green dot) and then the tip lowered to the molecule for mechanical interaction. As can be seen in Figure 3(C), the cluster has transformed into a new shape without losing C_{70} molecules. The arrangement of the cluster changes without changing total number of C_{70} molecules and Au atoms. It seems that the linear row of the three Au hexagonal islands has changed into a V-shaped row. A second manipulation event, Figure 3(E), has caused further changes to the cluster. The three raised C_{70} molecules have become close-packed, Figure 3(F). This suggests that the three hexagonal Au islands have fused together so that each hexagon shares two edges with other two hexagons. This is similar to the $(C_{60})_{12}-(Au)_{49}$ cluster. Since only 49 gold atoms to require for such a three-hexagon configuration, there are thus two redundant gold atoms. The redundant Au atoms can escape the cluster altogether. However, based on the STM image in Figure 3(F), the two redundant Au atoms seem to be attached to one edge of a hexagon. The number of molecules has dropped to 12. A third manipulation, Figure 3(H), has caused the cluster to lose another molecule. Since all the molecules in the cluster have become close-packed with no gaps, the gold core now has 49 atoms. The further manipulation achieved to the $(C_{70})_7-(Au)_{19}$ cluster (see supplementary information SupFig.1).

Figure 3: Manipulation of selected C_{70} molecules by one by in the $(C_{70})_{13}-(Au)_{51}$ hybrid cluster by the STM tip at room temperature. A, B and C show removing a single C_{70} molecule (indicated with a green dot) result in a metastable form similar to $(C_{70})_{14-1}-(Au)_{63}$ cluster with a missing C_{70} molecule. D, E, and F. Continues manipulation led to form $(C_{70})_{12}-(Au)_{49-51}$ cluster. H, I and J. Manipulation $(C_{70})_{12}-(Au)_{49-51}$ cluster to $(C_{70})_{12-1}-(Au)_{49}$ cluster. Following the cluster further, scale down to $(C_{70})_7-(Au)_{19}$ hybrid cluster (see supplementary information SupFig.1). Inset images show the atomic configuration of the cluster before (A) and after (D, G, I) manipulation.

Figure 4: Tip-triggered manipulation of $(C_{70})_{14}-(Au)_{63}$ cluster further down to $(C_{70})_{10+1}-(Au)_{35-49}$ cluster. A. STM image before manipulation and B-F. After manipulation images (see all images in supplementary information SupFig.2.)

Figure 4 demonstrates that another type of transition states occurs via the manipulation of $(C_{70})_{14}-(Au)_{63}$ cluster (see supplementary information SupFig.2 with before, during and after images). We were able to delicately trim $(C_{70})_{14}-(Au)_{63}$ cluster into a smaller cluster, the outcome was the $(C_{70})_{10-1}-(Au)_{35-49}$ cluster in this experiment. It can be seen from after images there is no cascade downsizing from one stable cluster to another. There is a high probability that the multiple phases of the hybrid cluster can be seen between two stable clusters, such as reshape, transition or interstate. The molecule on the top of the cluster also may diffuse on Au island and move to the cluster edge and fill the empty position of the frame without affecting the Au island shape. This is quite similar to tip-triggered C_{60} manipulation in $(C_{60})_m-(Au)_n$ at room temperature [8].

It is well known that individual/2D Au islands are not stable on the Au(111) terraces and they move to step edges via atomic diffusion above 240 K [25]. The stability of the 2D Au islands can be dramatically increased if the edges of the Au islands are decorated by C_{60} or C_{70} molecules. In the following, we describe the changes to 2D

Au islands when we remove C_{70} molecules from the step edges with the STM tip in Figure 5. In Figure 5 (A), there is Au island with its edges partially covered by 13 C_{70} molecules. The sequence of STM images of the ring cluster downsized by removing C_{70} molecules one at a time until there are just 5 molecules left. During manipulation, the island shape is disturbed each time and the island eventually formed a polygonal shape (A, B and C) with a direction of $[1\bar{1}0]$, $[11\bar{2}]$, and $[011]$, respectively. If all the molecules are removed from the cluster, the 2D Au island would not be stable. The Au island becomes stable when there are C_{70} molecules attached to the edges. It is not necessary to cover all the edges with the molecule. The island size can be defined with the number of C_{70} molecules. When we remove a molecule Au atoms in the islands do not leave the cluster. The fixed number of Au atoms in the cluster can have different geometry with similar energy value to increase the cluster components interaction [21]. The sudden change of C_{70} molecules orientation can be led to a new geometry without losing Au atoms.

Figure 5: Manipulation of individual C_{70} molecules around an open ring cluster. Removing a C_{70} molecules from $(C_{70})_{13}-(Au)$ cluster individually to $(C_{70})_5-(Au)$ cluster led to polygonal Au island appear with A, B, C directions refer $[1\bar{1}0]$, $[11\bar{2}]$, and $[011]$, respectively (see all images in supplementary information SupFig3).

A successful tip-induced manipulation event can be revealed via imaging half of the molecule and immediate change in the cluster. Although C_{70} displacement hard to determine, it usually undergoes rotation and removal from the cluster by the thermal energy of the surface [16]. We observed that once the cluster frame is broken via

the tip displacement on a selected molecule, it diffuses on the surface and attach a cluster, the step edges or stay around the cluster. The interaction among C_{70} molecules is the van der Waals interaction which is also responsible for the molecular displacement. Therefore, the right after manipulation the cluster can reshape or transform another cluster with an exact number of C_{70} molecules and Au atoms. Further removing C_{70} molecules result in inevitable Au atoms leave due to squeezing cluster components due to van der Waals force [19] so transformation or intermediate transition state may occur. This is an irreversible change and the new geometry of the cluster can be defined by the thermal energy of the surface or C_{70} orientations.

The experimental study and theoretical calculation showed that removing a selected C_{60} molecule from $(C_{60})_m-(Au)_n$ clusters resulted in a transformation which formed a down-sized the magic number clusters. Creating a vacancy in the cluster by STM-tip impact accumulate strain energy of the cluster and cause a release and diffusion of the C_{60} along with Au atoms in the cluster [7, 8]. This was due to the surface thermal energy and the minimum energy required holding the cluster components. The van der Waals interactions between C_{60} molecules relatively strong which led to bringing molecules closer so squeeze the island and transformed the cluster to one size smaller stable magic number cluster. Addressing the possible mechanisms underlying stability of the C_{70} -Au cluster is similar to C_{60} -Au clusters [7, 8, 18]. They are the molecule-molecule close-packing, the molecule-surface adatom, and molecule-2D Au island interactions. Although similar formations between C_{70} -Au and C_{60} -Au, the intermolecular differences play an important role in the cluster stability due to the rather weak interaction of Au(111) surface to C_{70} [23]. To obtain a close-packed arrangement with C_{70} molecules, the van der Waals force plays a significant role in the cluster stability [19]. Besides, the molecule on the top of the Au island contributes extra stability by interacting with all surrounding molecules as well as 2D-Au island in the cluster. Additional interaction between molecule and Au atoms enhance the cluster stability by transferring charge from the surface and 2D island Au atoms. For example, C_{70} charge transfer is 1.1 ± 0.1 electron/molecule [26] and for C_{60} 1.6 electron/molecule on the Cu(111) surface [27]. While the charge transfer from Au(111) to C_{60} is 0.8 electron/molecule [28], it is less for C_{70} which is observed experimentally [23].

Differently, for $(C_{70})_m-(Au)_n$ clusters the interaction between C_{70} molecules and Au- C_{70} relatively weak and removing a single C_{70} does not trigger cluster size to another small stable cluster. After the tip approach and

retract the pre-selected C_{70} molecule disappears and the number of Au atoms in the cluster usually remains constant until removal of another C_{70} molecule from the cluster. Therefore, the cluster is either reshape or transform to the intermediate transition state until another C_{70} removed from the cluster. Au atoms forced to leave the cluster when there is no place in the C_{70} cluster frame here molecule/molecule interaction become dominant thus the van der Waals force. The intermediate state of the cluster is energetically more favourite for molecules due to missing C_{70} molecule.

Our observation indicates that a simple repulsive interaction is responsible for the displacement of the C_{70} molecule without affecting other molecules and Au atoms. The created vacancy disturbs the interaction among the molecules which preferably stay in the cluster but the cluster obtains a new form. Further C_{70} extraction and migration away from the cluster result in losing Au atoms in the cluster so that the cluster can transform another stable cluster. When the tip does not accumulate sufficient energy on a selected molecule, the molecule may displace to a position, where less energy requires, and the cluster preserve the number of atoms/molecules but it is reshaped. The extracted molecule and atoms can be freely migrated on the surface until they are trapped by another cluster or the step edges of the (111) surface.

Conclusion

In conclusion, we used the high-resolution STM imaging/lateral manipulation method and achieved the tip-induced manipulation of a pre-selected C_{70} molecule without affecting other molecules/atoms in the $(C_{70})_m-(Au)_n$ clusters. The results of manipulation, which is a purely mechanical origin, showed that either an intermediate transition-states between the stable hybrid clusters or a transformation of the cluster occurred at room temperature. These states have preferably occurred either a weak interaction between C_{70} molecules and C_{70} -Au bonding or Au atoms in the 2D island but required sufficient energy to transform the cluster. Therefore, after tip approach/retract and induce stress on a selected molecule, the molecule can be removed and the components of the cluster stay in the frame until another C_{70} molecule moved away. We suggest that the van der Waals interaction among C_{70} molecules squeeze the cluster components and knockout the Au atoms from the island. These intermediate transition-states are due to van der Waals interaction and charge transfer between the

molecules and the surface. So achieving tip-induced manipulation, we can directly perturb a single molecule of a cluster to modulate its geometry, thus the electronic properties of the 2D molecule/atom clusters.

Author Contributions

D. K. and Y. W. performed all the experiments. All authors contributed to data analysis and writing of the manuscript. This work was supported by Cukurova University Scientific Research Funding Grand No: FBA-2018-10813.

Notes

The authors declare no competing financial interest.

REFERENCES

- [1] P. Jena, Q. Sun, Super Atomic Clusters: Design Rules and Potential for Building Blocks of Materials, *Chemical Reviews*, 118 (2018) 5755-5870.
- [2] K. Ariga, J. Li, J. Fei, Q. Ji, J.P. Hill, Nanoarchitectonics for Dynamic Functional Materials from Atomic-/Molecular-Level Manipulation to Macroscopic Action, *Advanced Materials*, 28 (2016) 1251-1286.
- [3] K.R. Rusimova, N. Bannister, P. Harrison, D. Lock, S. Crampin, R.E. Palmer, P.A. Sloan, Initiating and Imaging the Coherent Surface Dynamics of Charge Carriers in Real Space, *Nature Communications*, 7 (2016) 12839.
- [4] D. Lock, K.R. Rusimova, T.L. Pan, R.E. Palmer, P.A. Sloan, Atomically Resolved Real-space Imaging of Hot Electron Dynamics, *Nature Communication*, 6 (2015) 1-7.
- [5] T.L. Pan, P.A. Sloan, R.E. Palmer, Non-Local Atomic Manipulation on Semiconductor Surfaces in the STM: The Case of Chlorobenzene on Si(111)-7×7, *The Chemical Record*, 14 (2014) 841-847.
- [6] P.A. Sloan, S. Sakulsermsuk, R.E. Palmer, Nonlocal Desorption of Chlorobenzene Molecules from the Si(111)-(7×7) Surface by Charge Injection from the Tip of a Scanning Tunneling Microscope: Remote Control of Atomic Manipulation, *Physical Review Letters*, 105 (2010) 048301.
- [7] D. Kaya, J. Gao, M.R. Fard, R.E. Palmer, Q. Guo, Controlled Manipulation of Magic Number Gold–Fullerene Clusters Using Scanning Tunneling Microscopy, *Langmuir*, 34 (2018) 8388-8392.
- [8] D. Kaya, D.-L. Bao, R.E. Palmer, S. Du, Q. Guo, Tip-triggered Thermal Cascade Manipulation of Magic Number Gold-fullerene Clusters in the Scanning Tunnelling Microscope, *Nano Letters*, 17 (2017) 6171-6176.
- [9] E. Inami, I. Hamada, K. Ueda, M. Abe, S. Morita, Y. Sugimoto, Room-Temperature-Concerted Switch Made of a Binary Atom Cluster, *Nature Communication*, 6 (2015).
- [10] H. Kong, L. Wang, Q. Sun, C. Zhang, Q. Tan, W. Xu, Controllable Scission and Seamless Stitching of Metal–Organic Clusters by STM Manipulation, *Angewandte Chemie*, 127 (2015) 6626-6630.
- [11] A.O. Dmitry, G.K. Vasily, V.U. Tatiana, V.Z. Andrey, A.S. Alexander, The Manipulation of C₆₀ in Molecular Arrays with an STM Tip in Regimes Below the Decomposition Threshold, *Nanotechnology*, 24 (2013) 055302.
- [12] N. Martsinovich, L. Kantorovich, Modelling the Manipulation of C₆₀ on the Si(001) Surface Performed with NC-AFM, *Nanotechnology*, 20 (2009) 135706.
- [13] S.W. Hla, Scanning Tunneling Microscopy Single Atom/Molecule Manipulation and its Application to Nanoscience and Technology, *Journal of Vacuum Science & Technology B*, 23 (2005) 1351-1360.

- [14] S.-W. Hla, K.-F. Braun, V. Iancu, A. Deshpande, Single-Atom Extraction by Scanning Tunneling Microscope Tip Crash and Nanoscale Surface Engineering, *Nano Letters*, 4 (2004) 1997-2001.
- [15] G.E. Grazyna Antczak, *Surface Diffusion Metals, Metal Atoms, and Clusters*, Cambridge University Press, Cambridge, 2010.
- [16] M.J. Comstock, J. Cho, A. Kirakosian, M.F. Crommie, Manipulation of azobenzene molecules on Au(111) using scanning tunneling microscopy, *Physical Review B*, 72 (2005) 153414.
- [17] C.J. Murphy, D.P. Miller, S. Simpson, A. Baggett, A. Pronschinske, M.L. Liriano, A.J. Therrien, A. Enders, S.-Y. Liu, E. Zurek, E.C.H. Sykes, Charge-Transfer-Induced Magic Cluster Formation of Azaborine Heterocycles on Noble Metal Surfaces, *The Journal of Physical Chemistry C*, 120 (2016) 6020-6030.
- [18] Y.-C. Xie, L. Tang, Q. Guo, Cooperative Assembly of Magic Number C₆₀-Au Complexes, *Physical Review Letters*, 111 (2013) 186101.
- [19] A. Deshpande, H. Yildirim, A. Kara, D.P. Acharya, J. Vaughn, T.S. Rahman, S.W. Hla, Atom-By-Atom Extraction Using the Scanning Tunneling Microscope Tip-Cluster Interaction, *Physical Review Letters*, 98 (2007) 028304.
- [20] P. Maksymovych, J.T. Yates, Unexpected spontaneous formation of CO clusters on the Au(111) surface, *Chemical Physics Letters*, 421 (2006) 473-477.
- [21] Y. Wang, D. Kaya, J. Gao, Q. Guo, Stick-Sudden-Rotation and Structural Polymorphism of (C₇₀)_m-(Au)_n Hybrid Nanoclusters, *The Journal of Physical Chemistry C*, 123 (2019) 12791-12796.
- [22] G. Schulze, K.J. Franke, A. Gagliardi, G. Romano, C.S. Lin, A.L. Rosa, T.A. Niehaus, T. Frauenheim, A. Di Carlo, A. Pecchia, J.I. Pascual, Resonant Electron Heating and Molecular Phonon Cooling in Single C₆₀ Junctions, *Physical Review Letters*, 100 (2008) 136801.
- [23] Y. Wang, L.a. Guo, Q. Guo, Two-Component Fullerene Molecular Layers Assembled on the Au(111) Substrate, *The Journal of Physical Chemistry C*, 123 (2019) 7776-7785.
- [24] L. Bürgi, H. Brune, K. Kern, Imaging of Electron Potential Landscapes on Au(111), *Physical Review Letters*, 89 (2002) 176801.
- [25] M. Rokni-Fard, Q. Guo, Biased Ostwald Ripening in Site-Selective Growth of Two-Dimensional Gold Clusters, *The Journal of Physical Chemistry C*, 122 (2018) 7801-7805.
- [26] A. Goldoni, C. Cepek, R. Larciprete, L. Sangaletti, S. Pagliara, L. Floreano, R. Gotter, A. Verdini, A. Morgante, Y. Luo, C₇₀ adsorbed on Cu(111): metallic character and molecular orientation, *The Journal of Chemical Physics*, 116 (2002) 7685-7690.
- [27] C.-T. Tzeng, W.-S. Lo, J.-Y. Yuh, R.-Y. Chu, K.-D. Tsuei, Photoemission, near-edge x-ray-absorption spectroscopy, and low-energy electron-diffraction study of C₆₀ on Au (111) surfaces, *Physical Review B*, 61 (2000) 2263.
- [28] J. Hou, A. Zhao, T. Huang, S. Lu, C₆₀-Based Materials, in: *Encyclopedia of nanoscience and nanotechnology*, American Scientific Publishers, 2004, pp. 409-474.