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On-Surface Fabrication of Complex Hybrid Nanostructures

Huihui Kong, Likun Wang, and Wei Xu*

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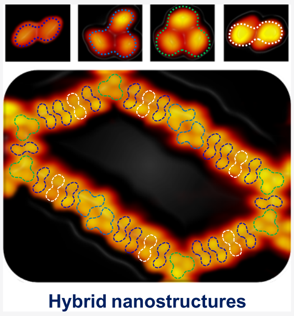
ABSTRACT: Complex hybrid nanostructures may integrate advantages of individual species and afford new functionalized materials with well-modulated properties for specific applications. In view of the potential distinctive nature of diverse metal−organic coordination structures, hybrid metal−organic systems composed of different elementary motifs would enrich the electronic and magnetic properties of the whole system. Herein, we propose a new strategy for the sample preparation, which results in the fabrication of complex hybrid nanostructures including several elementary structural motifs. This finding opens a new avenue for advanced fabrications of complex functionalized nanostructures, which may help for the rational design of novel nanomaterials and nanodevices.



■ INTRODUCTION

Bottom-up fabrication of desired surface nanostructures by precise control has attracted wide interests due to the potential applications in the fields of nanoscience and nanotechnology. In recent years, many efforts have been devoted to the construction of well-patterned molecular nanostructures through the cooperation and competition of non-covalent interactions, e.g., hydrogen bonds, coordination bonds, electrostatic ionic bonds, and van der Waals interactions.[1−5] Among others, fabrication of hybrid nanostructures composed of multiple components, such as host−guest systems, organometallic ones, metal−organic coordination ones, *etc.*, has been blooming as a hot topic, which may integrate advantages of individual components and exhibit improved properties or functions for specific applications.[6−11] The metal−organic coordination system is one of the typical representative hybrid systems,[9,11−16] wherein metal atoms could greatly improve thermal stabilities[12,15] of the nanosystems and enrich electronic/magnetic properties[13−16] in comparison with pure organic systems. By rational selection of organic ligands and metal atoms, a variety of metal−organic nanostructures have been realized.[9,11−24] Through regulation of the ratio of molecules and metal atoms or the thermodynamic equilibrium conditions (by reaching different local minima), various metal−organic motifs could be achieved;[25−27] however, fabrication of complex hybrid structures composed of several different motifs is still challenging. More recently, a kind of hybrid metal−organic nanostructure containing both f-metal and d-metal centers was reported.[11] It is therefore of general interest to develop strategies for fabrication of more and more complex hybrid nanostructures containing various elementary motifs.

Herein, we select a thymine (T) molecule and nickel (Ni) atom as a model system where Ni atoms are able to coordinate with T molecules for generating metal−organic motifs. In such a system, five elementary structural motifs with distinct stabilities could be formed on the Au(111) surface, as illustrated in Figure 1, which includes one hydrogen-bonded motif (**Motif 1**) and four sorts of metal−organic motifs (**Motif 2** to **Motif 5**). It would thus provide us an ideal system to explore the possibilities for the fabrication of hybrid surface nanostructures. By the traditional heating-up process after codeposition of T molecules and Ni atoms, these motifs could only be successively acquired through the thermodynamic

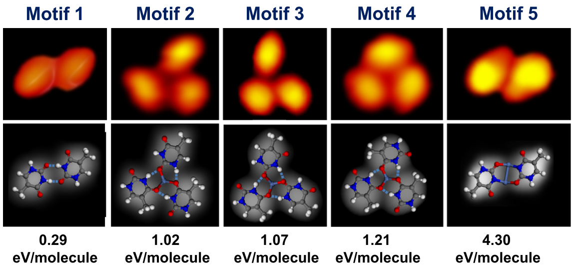


Figure 1. Schematic illustration showing the experimental STM images of elementary structural motifs formed by T molecules and Ni atoms (upper panel) and their simulated STM images with overlaid models (lower panel) as well as their corresponding calculated stabilities.

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phase transition on Au(111), as reported previously.[12,26] In the present study, we propose a cooling down strategy for the sample preparation, that is, by codeposition of T molecules and Ni atoms during natural cooling down of the substrate from a preheated status, up to four above-mentioned motifs could be simultaneously captured, which are further linked together by hydrogen bonds to form complex hybrid surface nanostructures.

■ EXPERIMENTAL SECTION

All scanning tunneling microscopy (STM) experiments were performed in an ultrahigh vacuum (UHV) chamber (base pressure, 1×10^{-10} mbar) equipped with variable-temperature, fast-scanning "Aarhus-type" STM,[28,29] a molecular evaporator and an e-beam evaporator, and other standard facilities for sample preparation. The Au(111) substrate was prepared by several cycles of 1.5 keV Ar^+ sputtering followed by annealing to 800 K for 15 min, resulting in clean and flat terraces separated by monatomic steps. The thymine molecule (purchased from Sigma-Aldrich with a purity >98%) was loaded into a quartz crucible in the molecular evaporator. A Ni wire (purchased from Mateck) was deposited by using an e-beam evaporator. After thorough degassing, thymine molecules and Ni atoms were sublimated onto the clean Au(111) surface held at certain temperatures. The sample was thereafter transferred within the UHV chamber to STM, where measurements were carried out over a temperature range of 120−150 K to stabilize the formed nanostructures. An electrochemically etched, polycrystalline W STM tip was used for collection of data. During the heating-up or cooling down process, the temperatures of Au(111) samples were detected by a thermocouple connecting on the manipulator stage.

The calculations were performed in the framework of density functional theory (DFT) by using the Vienna *ab initio* simulation package (VASP).[30,31] The projector-augmented wave method was used to describe the interaction between ions and electrons,[32,33] the Perdew−Burke−Ernzerhof generalized gradient approximation exchange−correlation functional was employed,[34] and van der Waals (vdW) interactions were included using the dispersion-corrected DFT-D3 method of Grimme.[35] The atomic structures were relaxed using the conjugate gradient algorithm scheme, as implemented in the VASP code until the forces on all unconstrained atoms were ≤ 0.03 eV/Å. The simulated STM images were obtained by the p4-vasp software based on the Tersoff−Hamann method.

■ RESULTS AND DISCUSSION

Deposition of T molecules on Au(111) held at room temperature (RT) leads to the formation of T islands composed of hydrogen-bonded **Motif 1** (with a binding energy of 0.29 eV/molecule) that are further bound together by additional hydrogen bonds within molecular chains (Figure 2a−c).[36] After introducing Ni atoms to the T islands at RT, a phase transition occurs and metal−organic **Motif 2** (composed of three T molecules and a Ni atom with a binding energy of 1.02 eV/molecule) appears (Figure 2d−f). **Motif 2** could either bind to itself or **Motif 1** by additional hydrogen bonds. Annealing the above sample to 370 K facilitates the formation of another kind of metal−organic chains composed of thermodynamically more stable **Motif 3** (with a binding energy of 1.07 eV/molecule, T/Ni ratio ∼3:1) (Figure 2g−i) or a hybrid network composed of **Motif 4** (with a binding energy of 1.21 eV/molecule, T/Ni ratio ∼5:1) and **Motif 1**

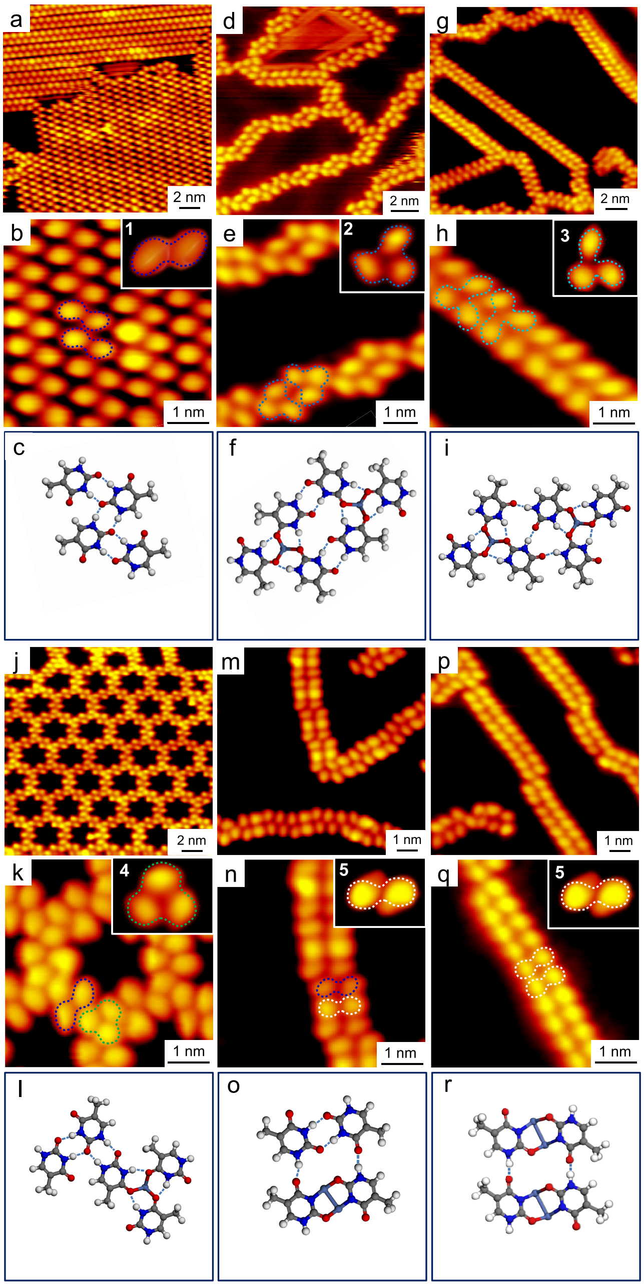

Figure 2. Large-scale, high-resolution STM images and optimized models of different phases involving distinct structural motifs (cf. the insets for **Motifs 1−5** with contours). (a−c) Self-assembled T island composed of a hydrogen-bonded T dimer (i.e., **Motif 1**). (d−f) After introduction of Ni atoms at RT, the self-assembled T island transforms to a chain structure composed of a metal−organic coordination trimer (i.e., **Motif 2**). (g−i) After annealing at 370 K (with sufficient Ni atoms), another kind of chain structure composed of a metal−organic coordination trimer (i.e., **Motif 3**) appears. (j−l) After annealing at 370 K (with sufficient T molecules), formation of a hybrid network structure composed of both a metal−organic coordination trimer (i.e., **Motif 4**) and **Motif 1** prevails. (m−o) After annealing at 390 K, a hybrid chain structure composed of both a metal−organic coordination dimer (i.e., **Motif 5**) and **Motif 1** appears. (p−r) After annealing at 410 K, the hybrid chain structure transforms to a pure metal−organic coordination chain composed of only **Motif 5**.

(Figure 2j−l), which could be interconverted and selectively achieved by providing additional T molecules or Ni atoms.[26] Further annealing the sample to 390 K results in the formation of hybrid chains composed of the most stable metal−organic **Motif 5** (with a binding energy of 4.3 eV/molecule) and **Motif 1** (Figure 2m−o). Finally, by annealing the hybrid chains to 410 K, the hydrogen-bonded **Motif 1** desorbs from the surface, and the remaining **Motif 5** constructs the pure metal−organic chains (Figure 2p−r).[12] Here, it should be noted that **Motifs 1**, **3**, **4**, and **5** have been systematically studied previously, and more details could be found in our previous work.[12,26,36] Thus, five sorts of elementary motifs have been successively acquired on Au(111) through the continuous phase transition induced by heating-up processes.

To preserve as many structural motifs as possible on the surface with an attempt to facilitate the fabrication of complex hybrid nanostructures, we propose a strategy for the sample preparation by codeposition of T molecules and Ni atoms during cooling down of the substrate from a higher temperature. By doing so, up to four above-mentioned motifs could be simultaneously captured and form hybrid structures on the surface. As shown in Figure 3a, by codeposition of T molecules and Ni atoms (deposition rates for T and Ni are 0.30 and 0.009 mL/min, respectively) on the surface during cooling down of the substrate from 450 to 380 K with a cooling rate of around 1 K/s, **Motif 1**, **Motif 4**, and **Motif 5** are simultaneously captured and complex hybrid structures with nanopores (an area of ∼19 nm^2) are achieved with a T/Ni ratio close to 3:1 in which **Motif 1**, **Motif 4**, and **Motif 5** with alternating arrangements are demonstrated by the contours in Figure 3a. More interestingly, further extending the range of substrate temperatures from 450 to 350 K with a cooling rate of around 0.9 K/s by codeposition of T molecules and Ni atoms (deposition rates for T and Ni are 0.19 and 0.005 mL/min, respectively), up to four structural motifs including **Motif 1**, **Motif 2**, **Motif 4**, and **Motif 5** are captured and form a more complex porous hybrid structure (with a nanopore area of ∼32 nm^2, T/Ni ratio close to 3:1), as shown in Figure 3b. As discussed previously,[26] as long as T molecules are sufficient (the T molecule/Ni atom ratio is higher than 3:1), **Motif 4** is energetically more favorable than **Motif 3** by linking with **Motif 1**; thus, it is not possible to construct a hybrid structure including all five motifs. It is also noticeable that these different motifs also have opportunities to form separate phases. In our previous study, the intermixed guanine-quartet structure is found to be stabilized by entropy compared to the homochiral one.[37] Similarly, we speculate that the intermixture of different motifs in this case would also lead to an increase of the entropy. As we know, the free energy $G = H - TS$, where H is the internal energy, T is the temperature, and S is the entropy. For the entropy, $S = k \ln\Omega$, where k is the Boltzmann constant, and Ω presents the thermodynamic probability. For the situation containing three kinds of motifs (Figure 3a), Ω should be $2^3 = 8$; the free energy would be lowered by 0.07 eV/molecule at its substrate temperature of 380 K. While, for the situation containing four kinds of motifs (Figure 3b), the free energy would be lowered by 0.08 eV/molecule at its substrate temperature of 350 K. Consequently, the intermixture of different motifs effectively lowers the free energy of the hybrid system and further facilitates the formation of hybrid nanostructures.

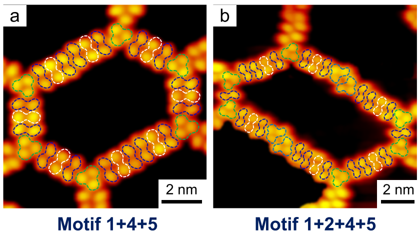

Figure 3. STM images showing the formation of hybrid nanostructures composed of **Motif 1** + **4** + **5** (a) or an even more complex one composed of **Motif 1** + **2** + **4** + **5** (b). The blue, indigo, green, and white contours indicate **Motif 1**, **Motif 2**, **Motif 4**, and **Motif 5**, respectively.

■ CONCLUSIONS

In conclusion, we have developed a strategy for the fabrication of complex hybrid surface nanostructures in which different kinetically trapped local minimum structural motifs are simultaneously formed. With respect to the general formation of thermodynamically more stable structural motifs by heating up the sample (to achieve phase transition), such a cooling down strategy for sample preparations allows us to achieve phase hybridization. It would be of utmost importance to employ such a strategy to more general systems, for example, involving different metals to fabricate multiple metal center structures that render further fundamental studies on their physical properties.

■ AUTHOR INFORMATION

Corresponding Author

Wei Xu − *Interdisciplinary Materials Research Center, Tongji-Aarhus Joint Research Center for Nanostructures and Functional Nanomaterials, College of Materials Science and Engineering, Tongji University, Shanghai 201804, P. R. China*; orcid.org/0000-0003-0216-794X; Email: xuwei@tongji.edu.cn

Authors

Huihui Kong − *Interdisciplinary Materials Research Center, Tongji-Aarhus Joint Research Center for Nanostructures and Functional Nanomaterials, College of Materials Science and Engineering, Tongji University, Shanghai 201804, P. R. China; Herbert Gleiter Institute of Nanoscience, School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, P. R. China*; orcid.org/0000-0001-5652-5269

Likun Wang − *Interdisciplinary Materials Research Center, Tongji-Aarhus Joint Research Center for Nanostructures and Functional Nanomaterials, College of Materials Science and Engineering, Tongji University, Shanghai 201804, P. R. China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcc.0c07993

Notes

The authors declare no competing financial interest.

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