Surface Nanostructure Formation and Atomic-Scale Templates for Nanodevices

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ABSTRACT: The holy grail in nanoelectronics is the construction of nanodevices with high density, low cost, and high performance per device and per integrated circuit. One approach is the fabrication of surface nanostructures and atomic-scale templates via the autonomous assembly of atoms and/or molecules on well-defined surfaces. To steer the atomic or molecular growth processes and create a wide range of surface nanostructures with desired properties, a comprehensive understanding of the mechanisms that control the surface self-assembly processes is required. The capability to manipulate the nanodevices at the submolecular level with good controllability is also of paramount importance. This review highlights some key recent developments in the fabrication of low-dimensional nanostructures based on supramolecular self-assembly on predefined surfaces, with particular emphasis on the rapidly expanding field of two-dimensional materials. Special attention is also given to the latest progress in single-molecule manipulation for future device applications.

1. INTRODUCTION

Nanostructured materials with length scales in the range of ~0.1–100 nm in at least one dimension are of great interest for their unique properties and potential applications in future nanodevices.† To build surface nanostructures and atomic-scale templates with desired functionalities, much effort has been allocated to understand and manipulate individual atoms and molecules on well-defined surfaces. Rapid developments in the field of nanoscience and nanotechnology have been achieved over the last 30 years or so with the invention and refinement of a variety of fabrication and characterization tools. Among various promising methods are included molecular beam epitaxy to fabricate well-ordered ultrathin films on surfaces and scanning probing microscopy to characterize spatial morphology and electronic properties with atomic resolution. A wide range of well-organized nanostructures have been fabricated, for example, isolated individuals/clusters, one-dimensional chains/ribbons, and two-dimensional (2D) extended networks, which can be used as quantum dots, high-density data storage media, sensors, spin valves, and so on.†‡§ When the dimension goes down to the nanometer scale, various physical phenomena, such as quantum confinement effects and surface/interface interactions, play critical roles in determining the electronic and optical properties of the nanostructured materials, which are significantly different from their bulk components. Therefore, the capability to construct robust and tunable nanostructures with varying sizes, shapes, and hence functionalities is required to fulfill the demanding requirements from various device types.

In this perspective, we will briefly review the latest progress in the fabrication and characterization of low-dimensional nanostructures on predefined surfaces based on supramolecular self-assembly. We will focus particularly on site-selective adsorptions on various surface templates, from the well-known Au(111)-(22×√23)-reconstructed structure to the new 2D materials including graphene, h-BN, and single-layer transitional metal dichalcogenides (TMDs) supported by metallic substrates with geometric and electronic corrugations (sections 2–4). We then discuss the surface-assisted synthesis of atomically precise graphene nanoribbons (GNRs) from small molecular precursors in section 5. Advances in scanning...
2. MOLECULAR SELF-ASSEMBLY ON RECONSTRUCTED SURFACES

Substrates with well-defined reconstructions can serve as templates for molecular self-assembly. As a prototype reconstructed surface, the Au(111)-(22 × √23) surface is composed of valleys, ridges, and elbows that result from alternating face-centered cubic (fcc) and hexagonal close-packed (hcp) regions. Previous works have shown the formation of various surface atom/molecule nanostructures mediated by the Au(111) reconstruction structure.5,9−15 Elegant examples are demonstrated in Figure 1b,e, where 4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine (SND) molecules16 (Figure 1a) and [30]trithia-2,3,5,10,12,13,15,20,22,23,25,30-dodecaaza-hexaphyrin (HTAP) molecules17 (Figure 1d) prefer to first reside at the elbow and then the valley of the Au(111) surface at low coverages. A clear hierarchy for selective adsorption is observable for the two coexisting elbow sites denoted as X and Y in Figure 1b, as the single SND molecules first decorate the X elbows, whereas the Y elbows remain free.

With advances in the combined STM/AFM techniques,18 investigations of single organic molecules on surfaces reveal better insights into local conformational changes. Figure 1c shows typical STM/AFM images of the SND molecule located at the valley (left column) and X elbow (right column), respectively. STM images do not reveal drastic differences; however, the corresponding AFM images clearly show a conformational change and suggest a variation of the interactions between the SND pyridine units and the underlying Au atoms at different adsorption sites. As such a subtle interplay between the molecular adsorption and the underlying surface potential governs the diffusion processes as well as the friction forces of complex molecules at surfaces, such investigations could help facilitate the design for future molecular nanovehicles.19,20

The Au(111) reconstruction can also template the long-range ordering of the adsorbed molecules.9,17 In Figure 1f, HTAP molecules align into one preferred orientation in the fcc or hcp regions as the molecular coverage increases, and the supramolecular orientation alternates the neighboring fcc and hcp regions, as highlighted by the green and blue triangles, respectively. The long-range orientational self-assembly is stabilized by S···H intermolecular hydrogen bonding as well as molecule−substrate interactions.

Other notable well-ordered molecular arrays engineered by the site-specific interactions between the adsorbed molecules and the periodically reconstructed substrates are shown in Figure 2. Figure 2a shows a nanomesh template formed on the 6H−SiC(0001) surface upon annealing. The quasihoneycomb nanomesh corresponds to the 6√3 × 6√3R30° reconstruction of a single graphene-like carbon layer partially covalently bonded to the truncated SiC surface.21−23 Upon deposition of 0.85 ML chloroaluminum phthalocyanine (ClAlPc) molecules, a well-ordered single-layer dipole array was observed on the SiC nanomesh, as shown in Figure 2b.24 As each ClAlPc exclusively adsorbs at the center of the SiC nanomesh holes in a Cl-up configuration, the intermolecular distance of ~1.85 nm is
determined by the underlying template, in contrast to that of 1.51 nm for the close-packed CIAPc on highly oriented pyrolytic graphite. The alignment of the CIAPc molecular dipole and the out-of-plane component of the surface dipole of the SiC nanomesh play a crucial role in the formation of the CIAPc nanoarrays.

In Figure 2d,e, the square $p(10 \times 10)$ reconstruction of Bi on Cu(100) enables the assembly of manganese phthalocyanine (MnPc) and copper phthalocyanine (CuPc) molecules into a chessboard pattern. The CuPc molecules prefer to adsorb at the pore sites (dark regions), whereas the MnPc (or cobalt phthalocyanine) molecules adsorb at the nodes (bright regions). The chessboard assemblies are mainly driven by the site-specific interactions between the central transition-metal ions of the Pc molecules and the reconstructed Bi template.

3. MOIRE PATTERNS IN SINGLE-LAYER GRAPHENE AND h-BN

Periodic moiré patterns formed in 2D layered crystals on a supported substrate can also serve as a template for nanostructure formation. Figure 3a represents a prototype moiré superstructure induced by the lattice mismatch between a single-layer graphene (Gr) and the Ru(0001) substrate. The three distinct regions are defined as top (triangle), fcc (orange hexagon), and hcp (blue hexagon). The graphene–metal distance varies significantly from the fcc/hcp sites (~2.1 Å) to the top sites (>3.6 Å) and thereby the graphene–metal interactions, which together result in a corrugation of the surface electronic potential of over 0.3 eV across the moiré unit cell. Such significant geometric corrugation and periodic electronic modulation are usually formed in graphene as well as h-BN monolayers grown on strongly interactive metals and play an active role in the molecular assembly.

Figure 3b reveals the site-selective adsorption of iron phthalocyanine (FePc) molecules on the Gr/Ru(0001) hexagonal moiré pattern. The molecules first adsorb on the fcc region at low coverage. As the coverage increases gradually, the molecules subsequently grow along the top fcc edges, followed by a filling of the hcp regions. As a result, a Kagome lattice of FePc molecules on the epitaxial Gr/Ru(0001) surface is formed in Figure 3c with the top regions remaining unoccupied. Combined with theoretical density functional theory (DFT) calculations, the coupling of the polarized Pc molecules to the surface dipole of the corrugated Gr/Ru(0001) moiré pattern is suggested to dominate the hierarchical supramolecular assembly to maximize the adsorption energy.

The assembly of 7,7,8,8-tetracyanoquinodimethane (TCNQ) molecules on Gr/Ru(0001) demonstrates similar site-selective adsorption, where the fcc/hcp regions are first decorated. However, the driving mechanism is different from the dipole mediation for FePc as discussed above. As a strong electron acceptor with low electron affinity, TCNQ tends to adsorb at the lower part of the Gr ripples, where the electron density is higher and the local work function is lower, to facilitate surface charge transfer. When the coverage increases to a full monolayer, the molecules assemble into well-ordered close-packed molecular arrays. As shown in Figure 3d, the TCNQ monolayer on Gr/Ru(0001) contains two distinct features, with the brighter features at top sites. Further investigations confirmed that the TCNQ molecules adsorbed at top sites are neutral, whereas the ones at fcc/hcp sites are negatively charged and give rise to Kondo resonance. Additionally, the spin-polarized $dI/dV$ spectra taken at the different molecular domains (Figure 3e) reveal the existence of magnetic contrast because of the formation of long-range magnetic order in the TCNQ monolayer, which might have potential applications as a spin filter or polarizer.

Monolayer h-BN as a nanotemplate for molecular assembly has also been carefully studied. Analogous to graphene, the h-BN single layers grown on metal substrates also exhibit selective adsorption of molecules because of the presence of a hexagonal moiré pattern. Figure 3f demonstrates that MnPc molecules are selectively trapped on the pores of the h-BN/Rh(111) ripples. Three types of MnPc with different topographic characteristics can be identified, as highlighted by the red, blue, and yellow circles. Detailed investigations and DFT calculations verify that the different topographic signatures can be assigned to multiple charged and neutral molecular states with different energy-level positions, which significantly depend on the adsorption site and orientation of the MnPc molecules with respect to the h-BN moiré surface.

Similarly, free-base porphyrin (2H-P) and TCNQ also exhibit preferential adsorption behavior on the h-BN/Cu(111) surface. A highly ordered array of the 18-2H-P-molecule clusters forms at the coverage of ~0.4 ML, as shown in Figure 3g. The superstructure with a periodicity of 7 nm is identical to the underlying h-BN/Cu(111) moiré template. When the coverage exceeds 0.4 ML, the 18-molecule clusters disintegrate and the 2H-P molecules form extended highly ordered porous networks with a periodicity of 3.2 nm (Figure 3h). Obviously, the template effect is overridden when the number of molecules is high enough.

The formation of molecular nanostructures on such 2D moiré patterns is actually complicated and varies from molecule to molecule.
to molecule and material to material, as they are determined by the weak interactions between the molecules and the substrate.\textsuperscript{27} No preferential adsorption is observed when the surface potential corrugation of the moiré patterned substrates is very small.\textsuperscript{40,41} This observation is also consistent in other 2D materials including TMD monolayers supported by the underlying substrates.

4. 2D TMD-PATTERNED MONOLAYERS

Atomically layered TMDs are the latest member of the 2D family, and relevant studies of self-assembly are still at their infancy compared to that of graphene and h-BN. Among the limited number of published studies, a well-ordered closed-packed perylenetetracarboxylic dianhydride array has been fabricated on a single-layer WSe\textsubscript{2} atop graphite substrate, and the molecular highest occupied molecular orbital–lowest unoccupied molecular orbital gap is enlarged by the WSe\textsubscript{2} interlayer because of the reduced dielectric screening of the monolayer TMD.\textsuperscript{42} Another study on C\textsubscript{60}F\textsubscript{48} (fluorinated fullerene) assemblies reveals a surface liquid to solid phase transformation with the increased molecular coverage.\textsuperscript{43}

Figure 3. Templating effect of graphene and h-BN moiré patterns. (a) High-resolution image showing a hexagonal moiré pattern of Gr/Ru(0001) with three distinct regions, top (triangles), fcc (orange hexagon), and hcp (blue hexagon). (b) FePc molecules first adsorbed at the fcc regions at low coverage, and (c) formed a supramolecular Kagomé lattice at sufficiently high coverage. (d) TCNQ monolayer on the Gr/Ru(0001) surface comprises two kinds of TCNQ molecules: neutral and charged. (e) Spin-polarized $dI/dV$ spectra recorded at the left and right domains of (d) reveal the long-range magnetic order in the organic layer on graphene. (f) Adsorption of MnPc molecules within the pores of h-BN/Rh(111). Three different types of MnPc can be identified. (g) Formation of a highly ordered array of 2H-P islands is confined by the h-BN/Cu(111) moiré pattern at 0.4 ML. (h) 2H-P molecules assemble to an extended porous Kagomé network at high molecular coverage, overriding the templating effect. (a,b) Reprinted with permission from ref 28; (c) from ref 31; (d,e) from ref 33; (f) from ref 38; and (g,h) from ref 39.

Figure 4. (a) Monolayer 1H/1T PtSe\textsubscript{2} on Pt(111) shows a triangular pattern constructed by alternating 1T and 1H domains. (b) Pentacene molecules selectively adsorb on the 1H phase region of PtSe\textsubscript{2}. (c) Enlarged STM image of a triangular molecular cluster. (a–c) Reprinted with permission from ref 45.
isolated C₆₀F₄₈ individuals is triggered by the repulsive intermolecular interaction induced by interfacial charge transfer, which has nothing to do with site-selective adsorption. The studies also indicate that the deposition of organic molecular layers on 2D materials is a promising approach to modify their electronic properties.

A prototype TMD monolayer with an intrinsically patterned structure was fabricated by Lin et al.—1H/1T PtSe₂ monolayer on a Pt(111) substrate grown by direct selenization in a poor Se environment. The atomic-resolution image in Figure 4a shows the triangular pattern of monolayer 1H/1T PtSe₂ constructed by alternating 1T and 1H phases. Interestingly, when pentacene molecules are deposited, they are selectively adsorbed within the 1H domains to form well-ordered triangular clusters (Figure 4b,c). As the 1T and 1H phases of TMD materials usually possess different electron densities as well as chemical reactivities, it is no surprise that the patterned 1H/1T PtSe₂ monolayer can be utilized as a template for molecular self-assembly. In principle, such preferential adsorptions of selected molecular species to one specific domain could be used in dual functionalization for catalysis or other applications.

5. GNRS FABRICATED BY MOLECULAR PRECURSORS

Molecular self-assembly on surfaces can also be harnessed to synthesize unique low-dimensional nanostructures with useful properties. Among various approaches to make the zero band gap graphene semiconducting, the most promising is the fabrication of GNRS which can behave as either a metal or a semiconductor depending on their widths and/or edge structures. Compared to many top-down methods such as lithography or unzipping carbon nanotubes, bottom-up methods to synthesize GNRS from small molecular precursors have more advantages in atomically precise control with predefined structures and widths. For example, straight armchair-edged GNRS with various widths can be fabricated from 10,10′-dibromo-9,9′-bianthryl (DBBA) monomers on the Ag(111) surface with two-step annealing (Figure 5a–e), by the linear coupling and surface-assisted cyclohydrogenation. Predefined by the molecular precursor, 7-, 14-, and 21-GNRS can be formed, where the numbers denote the number of carbon atoms in the direction perpendicular to the GNR axis. The STM image in Figure 5e reveals the different electron scattering patterns observed in the 7- and 21-GNRS induced by the width-dependent electronic structures. Such width-depend-
ent phenomena arising from the quantum confinement effect have been widely explored in both theory and experiment.\textsuperscript{55–58} A variety of GNRs, such as chevron-type GNRs,\textsuperscript{59,60} junctions,\textsuperscript{52,57,61,62} as well as N- or B-doped GNRs,\textsuperscript{63–65} have been fabricated by different molecular precursors. Figure 5f–h shows an elegant example of the synthesis of boron-doped GNRs (B-GNRs) by an organoboron precursor on the Au(111) surface.\textsuperscript{64} After annealing at an elevated temperature (510 °C), B-GNRs with various widths were obtained by the fusion of the armchair edges (Figure 5g). In Figure 5h, the chemical and structural properties of the B-GNR are well-resolved by a combination of high-resolution STM and AFM techniques, revealing a doping density of 4.8 atom %. Such substitutional doping GNRs further demonstrate higher chemical reactivity compared to that of the nondoped ribbons. This indicates that the low-dimensional carbon-based materials with better device performance and wider applicants are achievable by proper functionalization.

6. TOWARD DEVICE APPLICATIONS

The ultimate practical aim of the fabrication and investigation of nanostructures is the design of single-molecule-based functional devices using individual molecules as diodes, switches, data storage bits, magnets, or spin valves. The realization of such molecular devices largely depends on our ability to manipulate a single molecule between multiple conformational, chemical, electronic, or spin-valley states. Intensive research efforts have been devoted to trigger and understand the single-molecule operations by various external sources, such as light, temperature, electric/magnetic field, inelastic tunneling electron, and so on.\textsuperscript{66} The CIAIPc molecule represents a prototype nonplanar molecule, which possesses two distinct electric dipole configurations on a surface, namely, Cl-up ("1") and Cl-down ("0"), as shown in Figure 6a. In 2012, Huang et al. demonstrated that a reversible switching between the Cl-up and the Cl-down configurations with good controllability and repeatability can be realized in close-packed CIAIPc molecular arrays at 77 K.\textsuperscript{25} The switching direction is simply controlled by the polarity of the tip voltage pulses and the two states can be easily distinguished because the Cl-up state has a much brighter central protrusion (Figure 6b). This work demonstrates the capability of writing, reading, and erasing single binary bits of information with single-molecule precisions. Such ordered monolayer molecular dipole arrays can serve as an ultrahigh-density storage device with the capacity of around 40 Tb/cm\textsuperscript{2}. In 2014, Zhang et al. further demonstrated that the molecular bit density is tunable by a controlled deposition of a guest molecule, that is, perfluoropentacene (PFP), into the CIAIPc dipole arrays.\textsuperscript{67} Various binary networks were fabricated with different binary molecular ratios, for example, Figure 6c shows a CIAIPc/PFP network with a ratio of 1:2, and Figure 6d,e shows another with a ratio of 1:1. Although the binary networks are stabilized by weak intermolecular hydrogen bonds between the neighboring CIAIPc and PFP molecules, reversible dipole switching is nevertheless well-controlled (Figure 6d,e).

In 2017, Li et al. presented a practical realization of signal transmission and processing at room temperature using in-plane molecular orientation as the information carrier.\textsuperscript{68} The proposed model for an AND logic gate is shown in Figure 6f. The operation is based on the fact that the tin phthalocyanine dichloride molecules adsorbed on the Cu(111) surface can rotate between two stable in-plane orientations, which are

Figure 6. (a) Schematic drawing shows the reversible single-molecule switching induced by STM tip pulses. (b) In the well-ordered CIAIPc molecular dipole arrays, the Cl-down molecules ("0") were switched from Cl-up molecules ("1") by positive voltage pulses, and the switch can be reversibly controlled by negative pulses. (c–e) Density of the single-molecular bits can be tuned and controlled by the deposition of a guest molecule, that is, PFP. The reversible switching is not affected by the neighboring molecules in the binary molecular network. (f) Model shows an AND logic gate and the operation of the proposed molecular device. (g) Demonstration of the manipulation process of the logic gate via the STM tip to input signals. The orientational information can be transferred from one molecule to another via effective intermolecular coupling along the molecular array at room temperature. (a,b) Reprinted with permission from ref 25; (c–e) from ref 67; and (f,g) from ref 68.
effectively coupled to each other via lateral intermolecular interactions along the molecular chains, and the orientations are controllable with STM tip pulses. As demonstrated in Figure 6g, when the “0” signal (∝ orientation) is input into either A or B molecule, the output obtained from Y is “0”; in contrast, when the “1” signal (γ orientation) is input into both A and B molecules, the output becomes “1”. As such, molecular logic gates, OR and AND, can be constructed and operated with good thermal stability at room temperature.

7. CONCLUSIONS AND OUTLOOK

In conclusion, surface molecular assembly is a promising approach for fabricating atomically precise nanostructures and templates with desired functionalities for applications in future nanodevices. We predict that there will be increasing research interest in supramolecular nanostructures formed on 2D materials because of their novel and tunable optoelectronic and other exotic properties. Organic 2D nanostructures allow us to harness the advantages of both 2D materials and organic semiconductors to create layered assemblies with unique functions for flexible devices. The selective deposition of organic molecular layers is also an efficient bottom-up approach to functionalize 2D crystals (e.g., selected strong organic dopants to tune the carrier type/concentration and the Fermi level position of graphene and 2D TMDs) for robust device applications. A comprehensive understanding of the chemical, geometrical, and electronic properties of such molecular nanostructures is now possible with the combination of atomically resolved STM and AFM techniques. More work is needed to identify robust molecular nanostructures which can perform useful operations at the atomic scale with high controllability.

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