

## Review Article

# Recent Progress in the Fabrication of Low Dimensional Nanostructures via Surface-Assisted Transforming and Coupling

Jinbang Hu,<sup>1</sup> Zhaofeng Liang,<sup>1</sup> Kongchao Shen,<sup>1,2</sup> Haoliang Sun,<sup>1</sup>  
Zheng Jiang,<sup>1</sup> and Fei Song<sup>1</sup>

<sup>1</sup>Shanghai Synchrotron Radiation Facility and Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201204, China

<sup>2</sup>Department of Physics, Zhejiang University, Hangzhou 310027, China

Correspondence should be addressed to Fei Song; [songfei@sinap.ac.cn](mailto:songfei@sinap.ac.cn)

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Polymerization of functional organics into covalently cross-linked nanostructures via bottom-up approach on solid surfaces has attracted tremendous interest recently, due to its appealing potentials in fabricating novel and artificial low dimensional nanomaterials. While there are various synthetic approaches being proposed and explored, this paper reviews the recent progress of on-surface coupling strategies towards the synthesis of low dimensional nanostructures ranging from 1D nanowire to 2D network and describes their advantages and drawbacks during on-surface process and phase transformations, for example, from molecular self-assembly to on-surface polymerization. Specifically, Ullmann reaction is discussed in detail and the mechanism governing nanostructures' transforming effect by surface treatment is exploited. In the end, it is summarized that the hierarchical polymerization combined with Ullmann coupling makes it possible to realize the selection of different synthetic pathways and phase transformations and obtain novel organometallic nanowire with metalorganic bonding.

## 1. Introduction

The complementary bottom-up method using surface-assisted covalent coupling has been wildly applied recently beyond conventional molecular self-assembly for low dimensional nanostructured materials, especially in carbon-based nanomaterials. Since graphene was first fabricated by mechanical cleavage in 2004 [1], it has greatly facilitated the research of low dimensional materials into a hot topic, because of graphene's novel properties such as zero band gap originated from the  $sp^2$  hybridized carbon-carbon (C-C) covalent coupling, and the tuning width of graphene nanomesh (GNM) [2] which shows potential application in semiconductor industry. Besides, other low dimensional structures or materials also exhibit novel characteristics, such as extreme mechanical performance discovered on carbene [3], room temperature superconductivity reported on C-based nanomaterial [4], and high hydrogen storage capability [5]. Based on this, nowadays, ever increasing methods have been proposed to fabricate controllable low dimensional

architectures on solid surfaces. In order to get tailored nanostructures, the condition and treatment of specified substrates have to be taken into account. Although it is not easy to well control the nanostructure at the atomic level, there are indeed some efficient measures to improve the quality of synthesized nanostructures. Based on the recent progress, this review paper is devoted to summarizing the recent progress on certain types of on-surface fabrication and transformation and providing novel insight on synthetic routes to obtain low dimensional materials.

On-surface coupling can be activated in different ways in relation to the figure of substrate, the environment, and the selected molecular precursors, leading to the high diversity of low dimensional nanostructures. Overall, the strategies applied to synthesize atomically thin two-dimensional nanosheets can be divided into two parts: on-surface approaches and solution synthesis. Though the process in solution has an obvious advantage that all the covalent bond formations formed are irreversible, the deficiency shows in a lot of aspects, such as hardness to direct monomers into

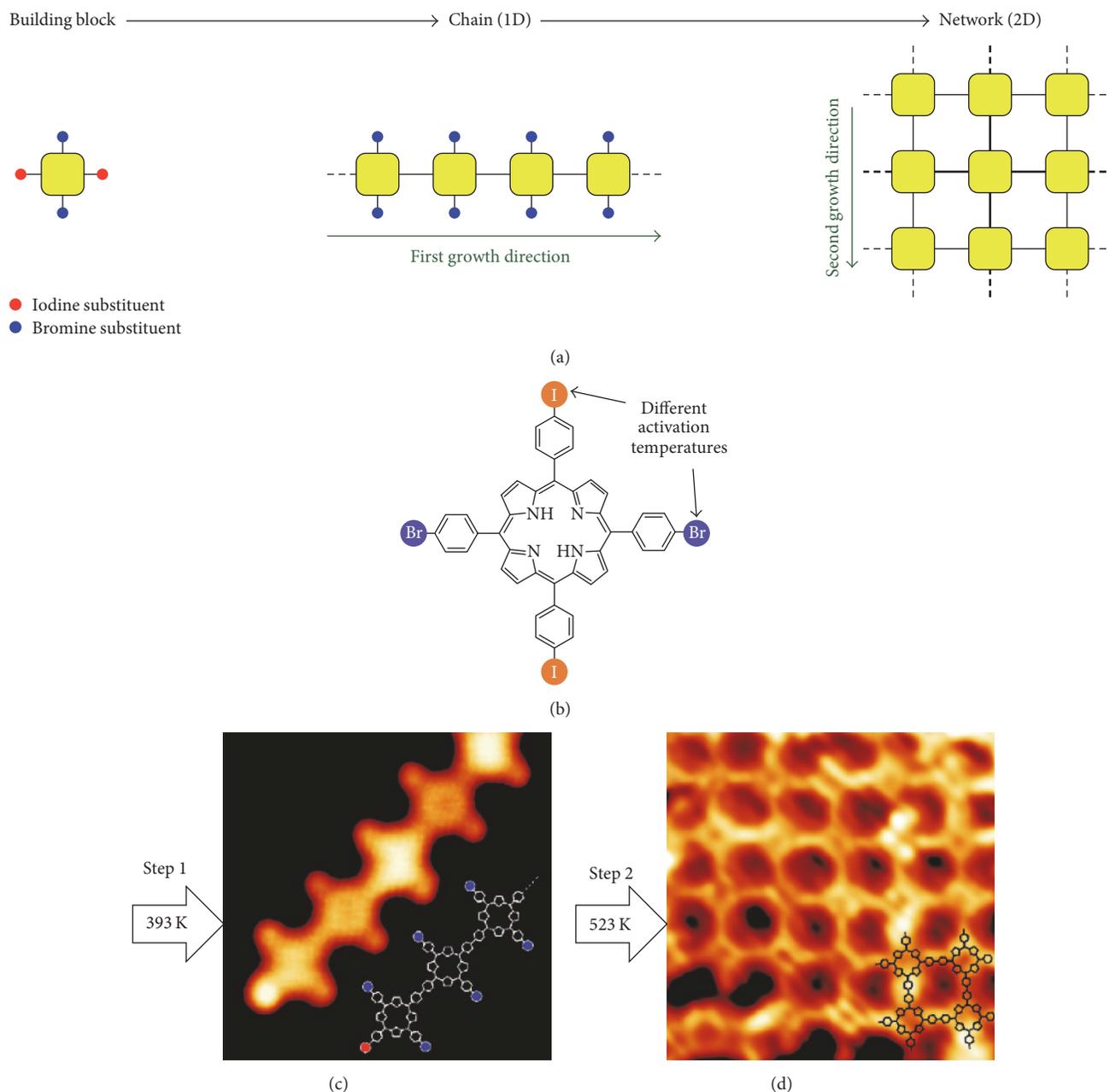


FIGURE 1: (a) Scheme of a hierarchical coupling strategy. Chemical structures of (b) trans-Br<sub>2</sub>I<sub>2</sub> TPP. Scanning tunneling microscopy (STM) images of (c, d) trans-Br<sub>2</sub>I<sub>2</sub> TPP molecules on Au(111) after deposition at 80 K followed by heating to 393 K (Step 1) and 523 K (Step 2). Figure was adopted from [6] with permission.

a two-dimensional geometry, the enormously fast loss of solubility with increasing size of the polymer, and the increase in lateral extension strongly hampering in isotropic solution experiments. In contrast, on-surface approaches not only rule out these disadvantages, but also make it possible to get rid of defects formed during the growth or bottom-up procedures. Bottom-up, one of interfacial approaches, is capable of controlling the supramolecular structure at atomic level. However, the reversible reaction turns out to be a sticky bottleneck for the on-surface approach. In fact, treatments of surfaces or substrates are crucial to remove the

byproduct stemming from the reaction on the surface and are likely to improve the quality of crystallinity of nanostructure, for example, hierarchical reaction route for the C–C coupling used for the monomer 5,15-bis(4'-bromophenyl)-10,20-bis(4'-iodophenyl)porphyrin (trans-Br<sub>2</sub>I<sub>2</sub> TPP) to form a two-dimensional 2D network, as shown in Figure 1 [6].

Moreover, different crystal phases are also obtained for the formed low dimensional nanostructures by tuning the reaction temperature due to the precursor's lateral movement on the surface, and different vibrational modes caused by further annealing lead to the discrepancy in atomic coupling [7].

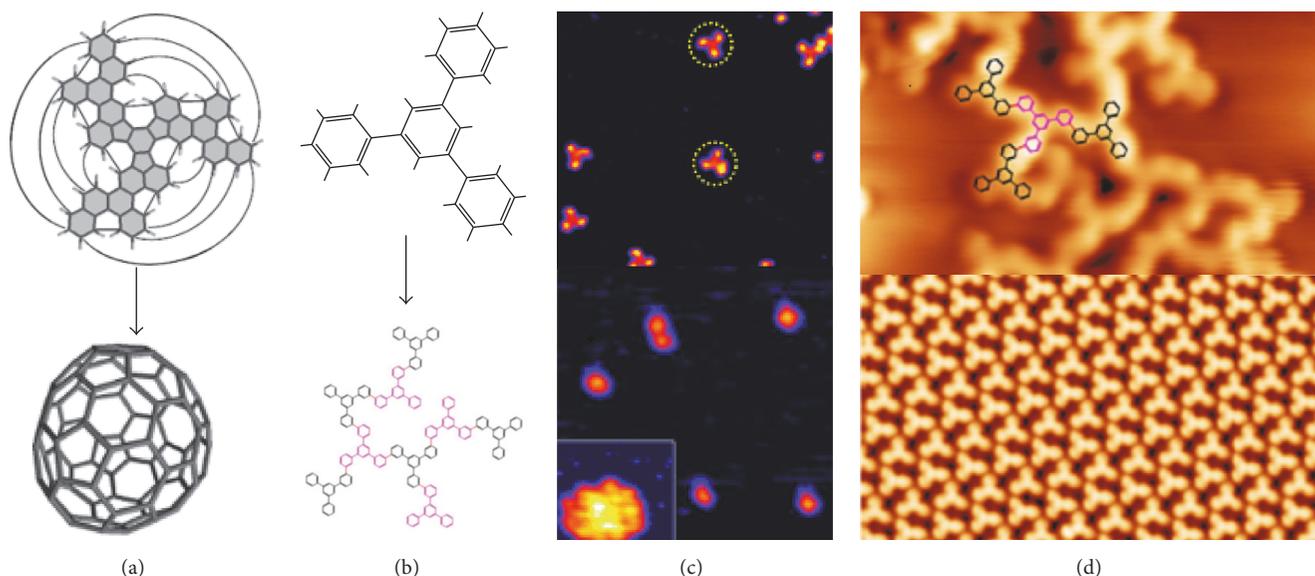


FIGURE 2: (a) Formation of  $C_{84}$  on Pt(111) by cyclodehydrogenation reactions of  $C_{84}H_{42}$ . (b) 1,3,5-Tris(4-hydroxyphenyl)benzene (THPB) oligomers obtained from THPB by dehydrogenation reactions on Ag(111). (c) STM images of the  $C_{84}$  cyclization process. (d) STM data confirm the coupling products THPB oligomers obtained by annealing at  $300^\circ\text{C}$ . Figures are adopted with permission from [8, 9].

Therefore interfacial approaches combining with deliberated design of the reaction process can get rid of the drawback, reaction reversibility, to realize high-ordered crystalline low dimensional nanostructures. Consequently, low dimensional materials obtained from on-surface approach have been widely reported among the world.

At this point, the outline for this review paper can be fixed in the following: First, several types of on-surface or bottom-up methods discriminated by the functionalities attached to the monomers are investigated. Nevertheless, factors, for instance, thermal treatment and surface energy, play an important role in the process of reactions; therefore it is of great significance to contribute discussion about them, which may give useful guides for experiments. Finally, attention is also paid to the Ullmann coupling because of its popularity in low dimensional nanostructure field with many novel discoveries.

## 2. Overview of Approaches and Discussion

As mentioned previously, there are several prevailing measures with coupling reactions for fabricating low dimensional nanostructures: dehydrogenation reaction, Schiff-base coupling, boron condensation reaction, and Ullmann coupling. After the examination of the principle and characteristics of these coupling reactions in sequence, optimized hierarchical polymerization obtained by combining advantages of the discussed coupling reactions is proposed in the end, aiming at the synthesis of nanostructures in a well controllable manner.

**2.1. Dehydrogenation Reaction.** Graphene, as a rapidly rising star on the horizon of materials science and condensed matter physics, features long-range  $\pi$ -conjugation and zero band gap, which result in remarkable in-plane carrier transport properties and attract numerous efforts to tune the band

gap towards its applications in semiconductor devices. Dehydrogenation reactions play an important role in fabricating graphene nanoribbons (GNR), of which energy band structures can be tuned by changing GNR's edge geometry and width [17, 18], and C–H bonds are the abundant functional groups present in organic molecules. Hence, the controlled activation of some special site's C–H bonds can lead to new promising synthetic pathways: dehydrogenation and cyclodehydrogenation reactions as shown in Figure 2.

The difference between these two reactions is that the requirement of geometrical morphology on cyclodehydrogenation reaction is stricter than dehydrogenation reactions in the process of cyclization, because the angle and distance need to be satisfied simultaneously during the cyclodehydrogenation. A typical example is that the surface-assisted reaction of planar polycyclic aromatic hydrocarbon precursor  $C_{84}H_{42}$  with well-designed structure (as shown in Figure 2(a)) [8] was induced resulting in cyclodehydrogenation reactions on Pt(111) at  $550^\circ\text{C}$ . According to the STM Figure 2(c), cage molecules  $C_{84}$ , a king of fullerenes, was obtained with the catalysis of Pt leading to cyclodehydrogenation reactions. This route for a surface-supported synthesis of fullerenes contains a topological transformation transforming the precursor into a closed spherical or quasi-spherical cage of the fullerene, which was firstly reported by Scott for formation of  $C_{60}$  on Ru(111) [10]. In fact, there are many kinds of low dimensional nanomaterials, especially like GNM and GNR, being fabricated with the help of cyclodehydrogenation reactions simultaneously having high atomic precision. Another type of C–C bond formed reaction is consequently dehydrogenation reactions without polycyclic aromatic hydrocarbon obtained. In Figure 2(b) [9], the possible process taking place on Ag(111) is 1,3,5-tris(4-hydroxyphenyl) benzene (THPB) getting dehydrogenated into oligomers, and STM image confirmed the

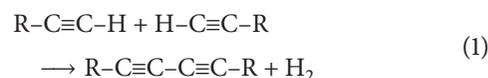
temperature-induced successive phase evolution from long-range ordered self-assembly structure to a thermally triggered surface chemical reaction, and the ordered structure of THPB monomers disappeared. However, the activation on C-H bond is at the same special site, ortho-C-H-bonds, leading to the ortho-ortho-coupling of THPB after annealing. During the process of polymerization, substrate not only is the support of nanostructured materials, but also acts as the catalyst improving the transformation of precursors. Unlike the previous mentioned cyclodehydrogenation reactions, bottom-up synthesis of dehydrogenative coupling usually produces organometallic intermediates at a relatively low temperature, for example, a successful on-surface synthesis of metalized carbyne chains by dehydrogenative coupling of ethyne molecules and copper atoms on a Cu(110) surface [19]. However, the bond between C and Cu atom is less stable than C-C coupling bond when the substrate with the metalized carbyne chains is annealed to a higher temperature. After that, a comparatively stable C-C coupling nanostructure would be obtained. This sort of stability is more likely to have a connection with the molecules' vibrational mode depending on temperature.

C-H bond occupied quite a bit of quantity in the monomers, and it can be activated to form polymers with abundant configurations, which improves the possibility of fabricating desired low dimensional nanostructure through accurate control of the surface condition. However, dehydrogenation reaction between porphine and edge of graphene occurs following different reaction pathways depending on the catalysis of substrate (Figure 3(a)) [10], because different reaction pathways may be activated at the same time with no obvious discrepancy in trigger temperature. Compared to the desired route modeled in Figure 3(b), unexpected dehydrogenation between porphines also occurred (shown on the top of Figure 3(a)), and the AFM data exhibits 4 kinds of coupling phenomenon with the corresponding model on bottom, leading to the ragged edge of the oligomers (Figures 3(c) and 3(d)). Different carbon site on molecules appears as discrepant symmetry, resulting in nuanced activation energy of C-H bond localized at the corresponding site. Plenty of efforts have been paid to explore how to avoid the undesired deformation. The deformation of polymers results from dehydrogenation reaction taking place at relatively different site of carbon seriously influencing their physical properties, but also polymers with irregular orientation confined on the surface would hinder the formation of long-range ordered polymers. Hence, there is inevitable requiring on exploration of the mechanism of surface-controlled selective C-H bond activation in order to successfully direct experimental fabrication [9].

In addition, the metal substrate not only serves as a support of low dimensional nanostructures, but also decreases the activation energy of dehydrogenation, leading to more participants in the process of coupling after C-H bond being separated [19–22]. On one hand, metal substrates decrease the relatively large bond dissociation enthalpy to let the action be easily done. On the other hand, cyclodehydrogenation reactions and dehydrogenation reactions may have selectivity of metal surfaces; for example, direct dehydrogenation

process inhibited on Au(111) or Cu(111) surfaces at room temperature has very low cycling efficiency of about 1% because of the negligible molecule-substrate interaction on these substrates [23, 24], while the efficiency on Pt(111) is amazingly high. Therefore, the importance of the substrate for catalyzing a specific chemical reaction is crucial. Due to the discrepancy of pathways in active temperature, the open-circle was formed if the annealing is hindered below the cyclization temperature, as verified by the following experiment: surface-assisted cyclodehydrogenation of  $C_{57}H_{33}N_3$  on Pt(111) while changing the temperature of annealing [24]. As a consequence, thermal control is undeniably a crucial factor.

Apart from the typical triply dehydrogenation actions, the main feature of Glaser coupling is to cleave C-H bond, a part of alkynyl. The process of the action can be schematically represented as



Glaser coupling has many similarities with dehydrogenations like C-H bond dissociation site, byproducts  $H_2$ , and the role of substrate as support of monomers and catalyst. Moreover, the effect of metal substrate was also tested: Ag substrate is comparably suited for Glaser coupling [25, 26], and Glaser coupling can be used highly efficiently to generate linear oligomer/polymer along the step-edges of the noble metal vicinal surface while inhibiting a variety of side-reactions resulting in irregularly branched polymeric networks [27]. Likewise, the defined  $\pi$ -conjugated two-dimensional network was realized after the optimization of the 2D Glaser coupling [28], while the precursor with more than 3 terminal alkynes is a determined factor.

Actually, polymerization reaction is not limited in the C-H bond, and it also occurs in other types of bonds like N-H bond [29, 30]. The greatest advantage of dehydrogenation reaction is that the byproduct H atom obtained during the C-H bond dissociation is easy to get rid of as  $H_2$  gas, so the quality of ordered nanostructure is hardly affected by H atom.

**2.2. Schiff-Base Reaction.** Apart from dehydrogenation actions, Schiff-base coupling is utilized to form extended polymeric low dimensional architectures on substrates by the usage of  $\pi$ -conjugated covalent bonding depending on two types of functional groups attached to monomers. Amine based monomers and aldehyde containing monomers undergo a reaction to create the repeat unit and byproduct  $H_2O$  (Figure 4(a)) [11]. The reaction can take place on different interfaces such as gas/solid or liquid/solid interface, and the solid substrate serves to support the polymerization reaction without strict limitation of materials. Nonmetallic substrate can also be used for Schiff-base coupling to obtain high-ordered polymers [11, 31, 32]. The methodology of Schiff-base coupling eliminates the strict reaction conditions for special nanomaterial and sophisticated equipment common to most current fabrication techniques and provides almost infinite

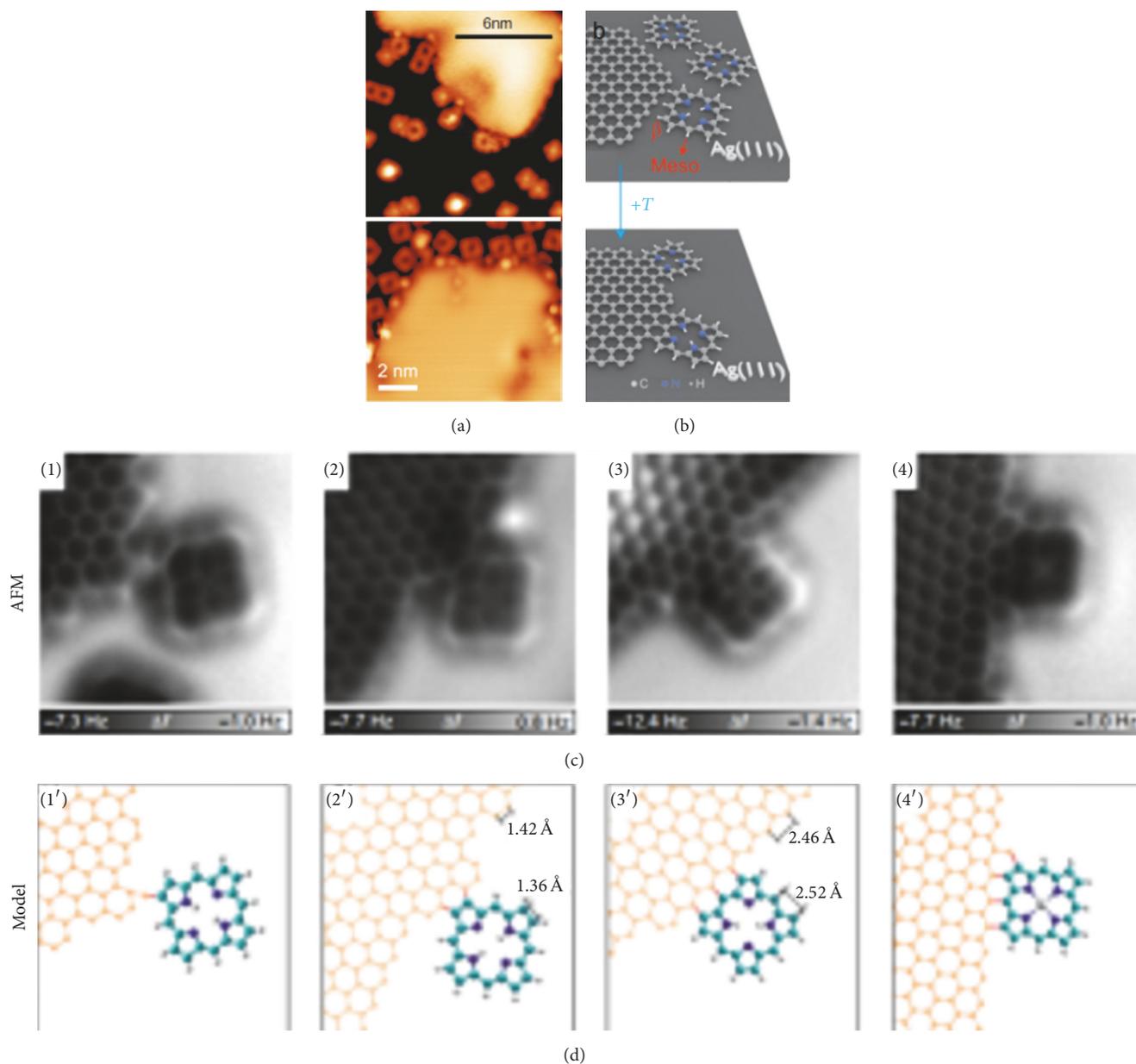


FIGURE 3: (a) STM images of dehydrogenation drove two different reaction pathways (reaction between porphines showed on the top, porphine and edge of graphene on the bottom). (b) Model of the process of dehydrogenation. (c–d) AFM images represent different C–C coupling ways of dehydrogenation with the corresponding models shown below. Images are reprinted with permission from [10].

possibilities for the preparation of large-scale monocrystalline nanomaterials with designed building blocks.

The condensation of Schiff-base coupling reaction on metal substrate confirmed the use of metal serving as catalyst [33], and diverse reactions and defect also occurred like dehydrogenation reactions. However, the diversity of interface shows the great influence on the order of nanostructure. For instance, Schiff-base coupling between terephthalaldehyde and p-phenylenediamine at the octanoic acid/HOPG interface leads to well-ordered assembly of the surface-confined one-dimensional polymers at the solid/liquid interface but on-surface coupling between isophthalaldehyde and p-phenylenediamine at the

gas/HOPG interface results in defective polymer domains (Figures 4(b) and 4(c)) [11], and the Schiff-base coupling under liquid environment can easily start at room temperature, while the reaction at gas/solid interface needs vacuum or proper pressure [11, 34, 35]. In addition, it is confirmed that the reaction rate of imination at the solid/liquid interface is  $10^4$  times faster than that in the solution [36]. Therefore, the reaction taking place on liquid/solid interface is more propitious for the obtained self-assembly nanostructure than on gas/solid interface.

In contrast to other similar polymerization reactions on the solid surface, the reversibility of Schiff-base reaction is a prominent advantage in on-surface synthesis of cyclic

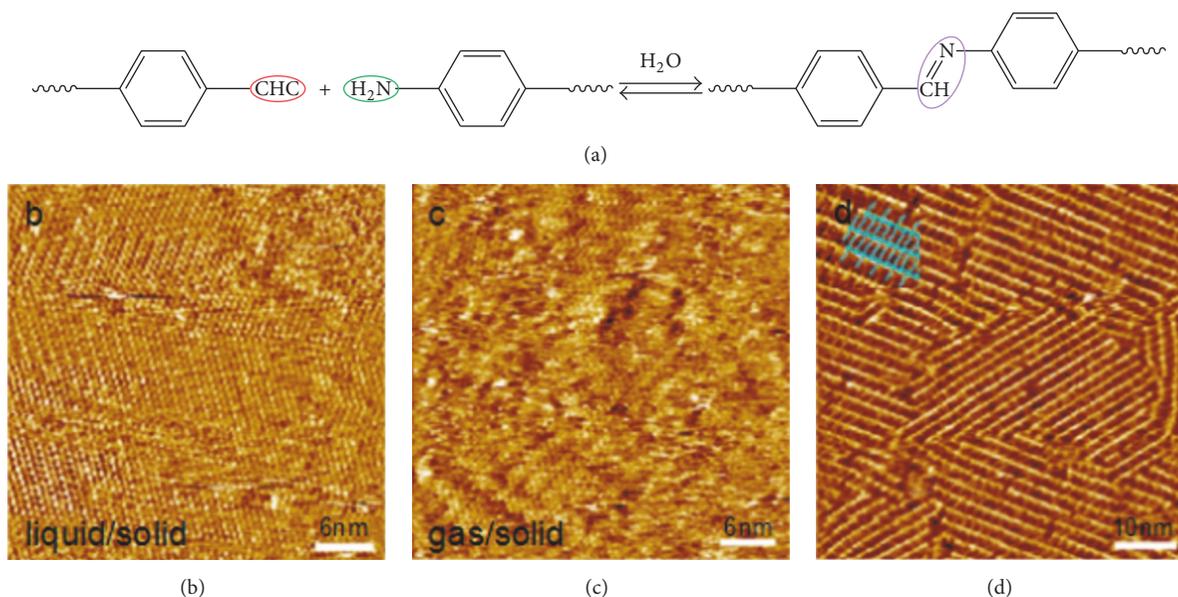


FIGURE 4: (a) Condensation reaction between aromatic diamine and dialdehyde. (b) STM images of Schiff-base coupling between terephthalaldehyde and p-phenylenediamine at the octanoic acid/HOPG interface. (c) Coupling between isophthalaldehyde and p-phenylenediamine at the gas/HOPG interface. (d) STM images of polymers derived from condensation of 2,5-bis(octyloxy)terephthalaldehyde and p-phenylenediamine. Figures are adopted with permission from [11].

organic molecules, which allows for the conversion of 2D self-assembled nanostructures into 2D covalent molecular networks. The reversibility of the Schiff-base reaction has big potential for growing large-scale LD nanomaterials, and this interesting property was further studied, as is shown in Figure 5 [12]. One typical example for the reversibility of Schiff-base reaction is the coupling between 5,10,15,20-Tetrakis(4-aminophenyl)porphyrin (TAPP) and terephthalaldehyde (TPA), where the covalent bond formation/cleavage dynamics was certainly demonstrated in detail. The reaction reversibility and diffusion ability of the monomers and formed polymers at the gas/solid interface are relatively low in comparison with those at the solid/liquid interface [11]. Moreover, the higher temperature may increase the reversibility of the reaction and also the diffusion rate of the building blocks [31]. Therefore, the rational use of thermodynamic control and reversibility gives more possibility of fabricating high-quality and large-scale polymers.

Another important investigation demonstrates that the polymerization of Schiff-base reaction can be delicately controlled using the pulse width, avoiding uncontrolled polymerization [33]. Combining with the alkyl group introduced to adjust the lattice constant and size of low dimensional nanostructure (Figure 4(d)) [11, 37], Schiff-base coupling reaction occupied a decisive position in the methodology of surface-enhanced polymerization of nanostructures.

**2.3. Self-Condensation of Boronic Acids.** Boron condensation reaction is a very popular synthesis approach to obtain covalent organic framework (COF) in which the building blocks are linked by strong covalent bonds. Unlike the reaction that occurred in solution, fabricating low dimensional COF at the liquid/solid or gas/solid interface through self-condensation

of boronic acids is a novel method to form a series of nanomaterials equipped with functional characteristics such as sensing [38, 39], energy storage [40], optoelectronic devices [41, 42], and catalysis [43, 44]. The building blocks of the condensation equipped with more than two functional groups, hydroxide radical, is a basic precondition to trigger the reaction, and the ambient environment around the reaction monomers can obviously decide the quality of the surface covalent organic framework (SCOF). The cyclic self-condensation of three boronic acids yields planar boroxine rings ( $B_3O_3$ ), and three  $H_2O$  molecules per boroxine ring are eliminated during the first stage of the polymerization, and subsequently self-condensation of diboronic acids gains covalent sheets with a hexagonal arrangement of boroxine rings that are interconnected by the organic backbone of the diboronic acid monomer. The mechanism of the self-condensation of boronic acids is showed in Figure 6, and the low dimensional COF formed by this method can be verified by both the monolayers' high thermal stability and the accompanying chemical changes by X-ray photoelectron spectroscopy (XPS) [13].

Apart from the condensation that occurred in the solution, cross-linking of molecules on solid substrates can yield single-layer 2D polymers owing to the confinement of substrate and removing the disturbance from the ambient environment. This 2D constraint at the interface has a crucial influence on the entropic contribution to the free enthalpy, because some rotational and translational degrees of freedom are suppressed, and furthermore it is the entropic contribution of the water molecules released during polymerization that leads to the boronic acid polycondensation and endothermic reaction.

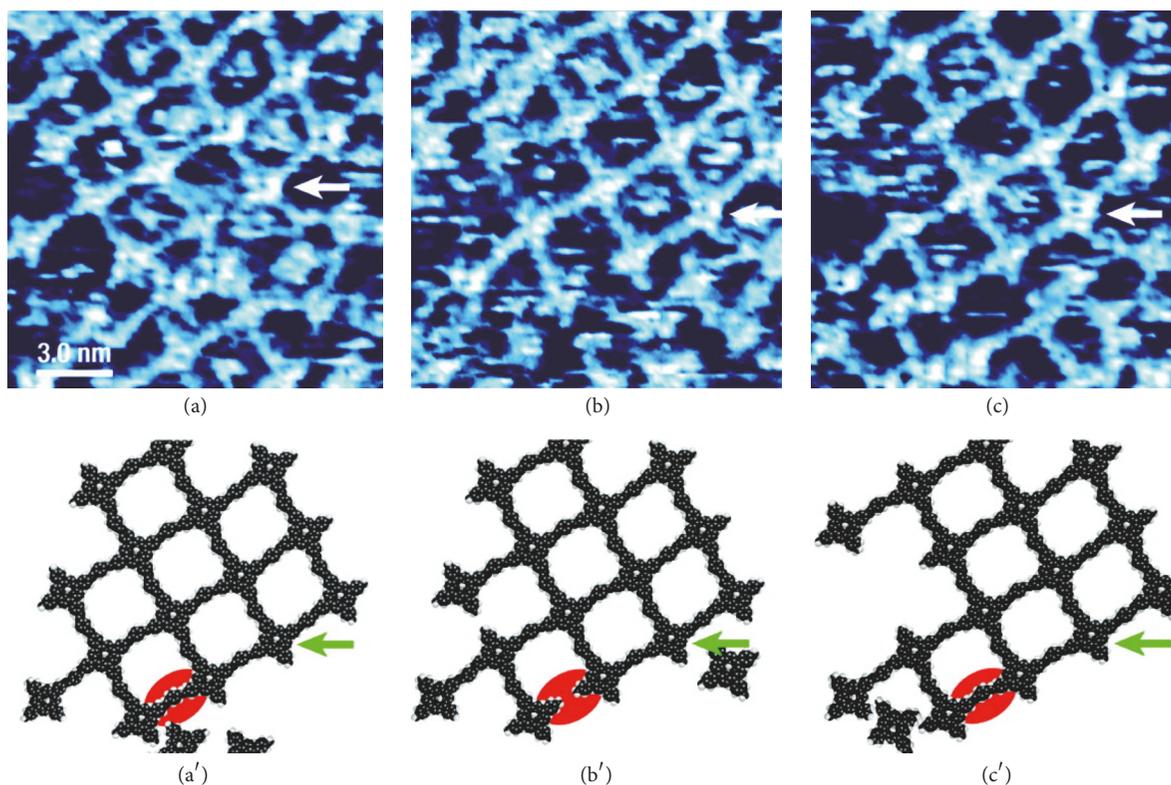


FIGURE 5: The condensation of Schiff-base coupling reaction occurred between TAPP and TPA, sequential (a–c) images acquired in the same location, and corresponding structural models (a'–c') clearly demonstrate covalent bond formation/cleavage dynamics. Figures are adopted with permission from [12].

Similar to Schiff-base reaction, one of the bright characters in this type of reaction is reversibility in the process of reaction depending on the amount of water around the COF. Increasing the  $\text{H}_2\text{O}$  molecules in the position where the condensation of boronic acids occurred or controlling the temperature of the reaction systems, the formed planar boroxine rings ( $\text{B}_3\text{O}_3$ ) can be triggered to separate into three monomers while 3  $\text{H}_2\text{O}$  molecules are being absorbed in the reaction. It is common that the defect formed in the large-scale LD nanostructure because of improper or imprecise control in precursor supplied or temperature acquired for the activation of B–O bond and H–O bond, and the imperfection interlinked in the SCOF shows the same morphological characteristics similar to the circumstances in other types of coupling mentioned above. Therefore, the reversibility in the process of reaction depending on the amount of water gives an opportunity to transform the domain with severe deficiency into regular crystalline SCOF. But how to use this advantage under the ultra-high vacuum (UHV) atmosphere to realize the precise control of fabricating polymers is still a challenge acquiring the optimism of method.

Compared to the reversibility of polymerization reaction, adjusting the size of porous structure embedded in the nanosheets through changing the straight organic backbones of the diboronic acids is another novel property for increasing the diversity of the nanostructure. Taking advantage of different monomers with alternative length of the straight organic

backbones in the diboronic acids, not only can the size of pore be changed, but also the figure of the planar boroxine rings can be transformed from one to another, such as the implemented scheme showed in Figure 6(d) that the condensation of boronic acids occurred between 1,4-benzenediboronic acid (BDDBA) and 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) simultaneously generating a five-membered  $\text{BO}_2\text{C}_2$  ring [45], being different with the formed planar boroxine rings ( $\text{B}_3\text{O}_3$ ). The lattice parameter and pore size of the 2D SCOF are obviously different leading to the discrepancy between two types of monomers, biphenyldiboronic acid and terphenyldiboronic acid, used for polymerization reaction (Figure 6(b)) [46]. Therefore, ignoring the long-range ordered characteristics of the polymers, the topological diversity of nanostructure can be used to tune the electronic property of SCOF. This general design principle of organic materials is popular in supramolecular monolayers [47, 48], isoreticular metal organic frameworks (MOF) [49], and 2D metal coordinated networks [50] and has also been exploited successfully for bulk crystals of various diboronic acid-derived COFs [51–53].

The reversibility of boronic acid polycondensation implies tremendous potential in fabricating large-scale crystalline SCOF. However, it is still hard to manipulate the process of polycondensation along the direction you want with the  $\text{H}_2\text{O}$  molecule supplied under the UHV systems. Reversibility means that the polymerization has to be carried out in a water atmosphere. Boron condensation reaction can

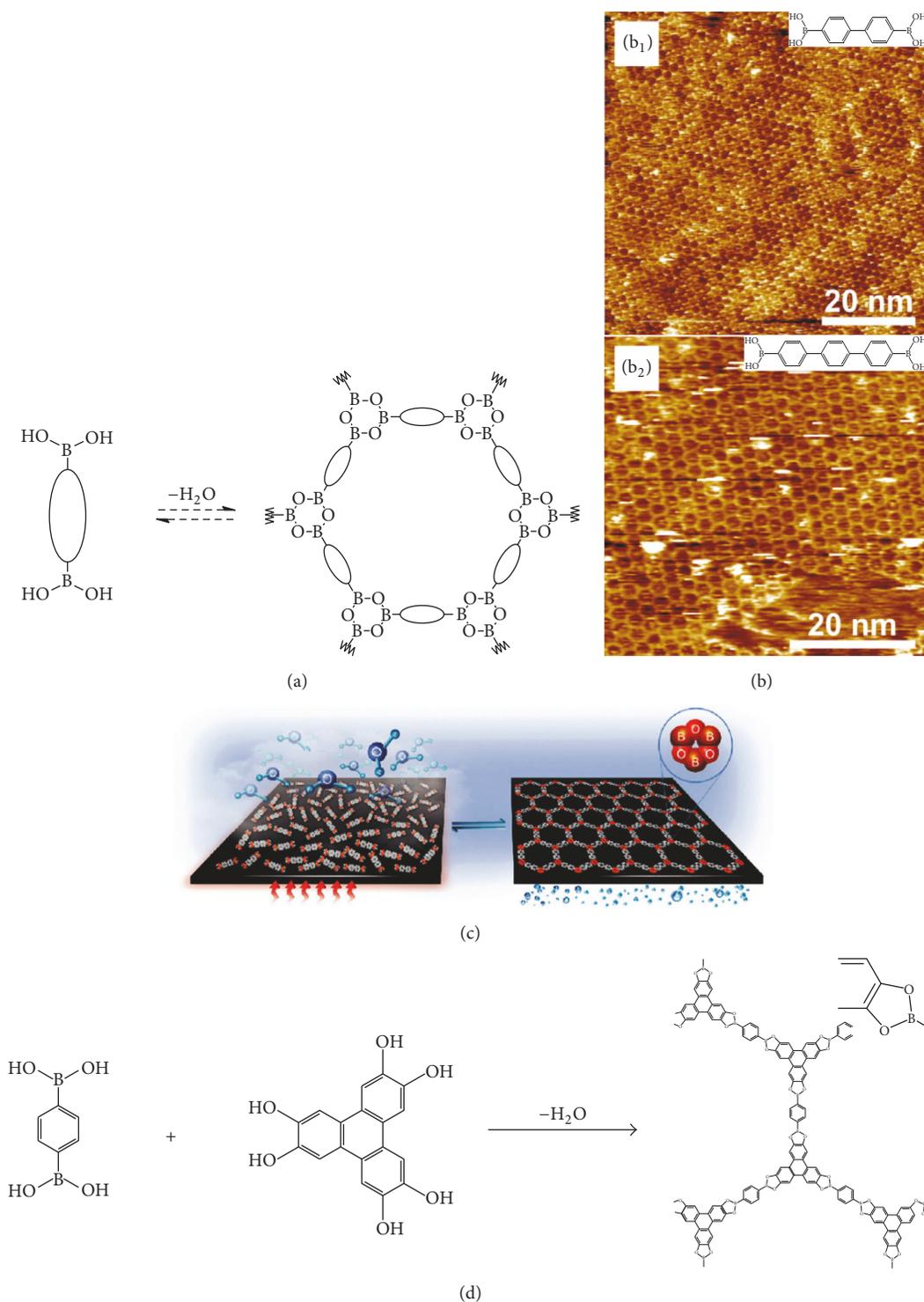


FIGURE 6: (a) Reaction scheme of the self-condensation of para-diboric acids into 2-dimensional (2D) COFs. (b) The methodology about different monomers used for the self-condensation ending in forming 2D nanonet with diversified size of porous structure inside. (c) The process of self-condensation of para-diboric acids controlled and regulated by means of water released or obtained to gain large-scale and high-ordered 2D nanosheet. (d) Another type of condensation of boronic acids occurred between diboric acid BDDBA and hexahydroxytriphenylene HHTP simultaneously generating a five-membered ring. Figures are adopted with permission from [13].

occur not only at the liquid/solid interface but also in UHV systems. However, the reversibility of polycondensation was disappearing if the reaction takes place at UHV systems without a certain amount of water molecules supplied. Because a water partial pressure in the order of  $10^{-6}$  mbar, the highest bearable in a UHV system, is not sufficient for activating the reaction along the reversible way, how to use this reversibility of the polycondensation under the UHV systems appears as an important problem in getting high-quality crystalline nanostructure.

To date, polycondensation on surfaces has already yielded promising results [54–56]. In particular, the condensation at liquid/solid interface depends on the reversibility or gas/solid interface in the closed systems while the water is being supplied by some novel path; for example, blue vitriol ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) reversibly releases part of its crystal water already around  $100^\circ\text{C}$  making it possible for removing the defects in long ranged ordered COF [57, 58]. As shown in Figure 6(c), the water molecules released from  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  during the heating process can act as an equilibrium-manipulating agent to push the dehydration reaction backward and thus promote defect remedy process to form a highly ordered network, and the water released from  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  would be reabsorbed to  $\text{CuSO}_4$  again during the cooling process and prevent the potential decomposition of SCOFs [46]. In other words, controlling the temperature of the reaction straightly related to the amount of  $\text{H}_2\text{O}$  supplied by the temperature-dependent and reversible dehydration of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . The situation in which surface monomers are self-assembled at the liquid/solid interface needs to be changed. In order to convert a noncovalent self-assembled monolayer into a surface-supported 2D COF, several different reacting steps, such as breaking up of hydrogen-bonded aggregates, surface diffusion, reorientation, and possibly desorption, need to be overcome. Thermal activation plays an important role not only in initiating the polycondensation but also in breaking up the preceding noncovalent arrangement, that is, the self-assembled monolayer [46]; meanwhile it can properly increase the surface mobility which is limited at room temperature leading to low degree of order in these kinetically trapped structures [59]. Besides the advantage of reversibility of B–O bond, the monomers dissolved eventually in solution can deposit on solid substrate at the same speed, which can prominently improve the quality of SCOF.

Apart from the condensation of boronic acids on the liquid/solid interface in an open system, the basic experimental conditions between UHV and the liquid/solid interface are extremely different and the interaction between monomers and metals is typically stronger; preceding supramolecular phases may play a general role in polymerization reactions of monomers that can also form relatively stable hydrogen-bonded structures [60]. This type of condensation can be activated under the UHV atmosphere at normal temperature without the requirement of thermal activation. Unlike the way of depositing monomers on the liquid/solid interface, evaporating is often used under the UHV atmosphere, and once the polycondensation has taken place, the formed surface network shows extremely high stability, because the extra-low amount of water causes the reversibility of the

condensation of boronic acids to disappear. The growth parameters (evaporation flux, substrate nature, and temperature) tightly associate with the quality of the obtained SCOF, and it has been explored to determine the experimental conditions that help to reduce all kinds of defects and produce optimum growth conditions for an ideal honeycomb network [60].

In conclusion, the methodology of condensation of boronic acids has been extremely developed [12, 58, 60–62] dating back to the job that both mechanisms and thermodynamics of the on-surface condensation of 1,4-benzenediboronic acid were already studied by density functional theory complemented by entropy considerations [60]. The reversibility of boronic acid polycondensation depending on water atmosphere decides that ambient conditions are the favorable environment to realize reversible reaction conditions and that the condition of reaction at the liquid/solid interface in the opened systems is relatively milder than UHV systems. However, the dispersion relation obtained from density functional theory (DFT) simulations suggests any 2D COF synthesized by boronic acid condensation will not be suitable as an electronically active material [63].

*2.4. Ullmann Reaction and the Optimization of Hierarchical Polymerization.* The wide requirement on highly stable and electronically conjugated networks in coupling chemistry establishes new C–C bonds which overcome the dielectric material formed by boron condensation reaction. Ullmann coupling is the most applied C–C coupling reaction and several studies have been applied to characterize the influence of the reaction conditions, the mechanism, and the electronic properties of each intermediate. Traditional Ullmann coupling reactions were pioneered by the work of Fritz Ullmann and Irma Goldberg in the early 1900s [64], and the solution-phase Ullmann coupling reaction was originally developed as a C–C coupling between aromatic halides induced by copper or Cu halide, a trend which continued to the end of 20th century. Afterwards, this type of coupling was transferred to solid surfaces (mostly coinage metals) in UHV for on-surface synthesis of 1D and 2D polymers [65], and the mechanism of the classical solution-phase Ullmann coupling reaction mechanism ( $\sigma$ -bond metathesis [66]) and the later reaction mechanism may be substrate- and molecule-dependent, also because the necessary reaction conditions vary with the substrate [67]. Two typical mechanisms are displayed in Figure 7.

The primary process of both mechanisms is similar dehalogenation leading to so-called surface-stabilized radicals (SSR), and the subsequently formed dangling bonds of the dehalogenated carbons bind to the underlying metal surface. However, the further progression of the coupling reaction appears rather differently, since the role of metal substrate changes with their species. The biggest difference between these two mechanisms is if the organometallic intermediates with C–M (metal)–C bonds exist. Actually, the scheme of this type of reaction is relatively straightforward: brominated or iodinated precursor molecules are deposited onto a metal surface, typically noble metal. Upon adsorption, the weakly bonded halogen substituents are split off with

TABLE 1: Dehalogenation of brominated versus iodinated precursors and occurrence of organometallic intermediates for different metal surface.

$d^{10}s^1$ metal	Bromine cleavage	Iodine cleavage
Cu(111) organometallic $\rightarrow$ disordered	Full @ RT	Full @ RT
Ag(111) organometallic $\rightarrow$ ordered	Partial @ RT Full @ $\sim 150^\circ\text{C}$	Full @ RT
Au(111) <i>rarely</i> organometallic intermediates	None @ RT Full @ $\sim 180^\circ\text{C}$	Full @ RT

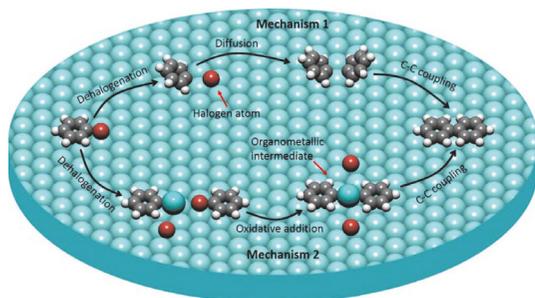


FIGURE 7: Two typical mechanisms are showed to simulate the process of the Ullmann coupling.

the aid of the catalytic properties of the metal surface, and the subsequently formed dangling bonds are coupled to be C-C bond through the mobility of the alkyl on the surface of metal in mechanism 1 as a direct way of establishing covalent bonds after the dissociation of C-X (halogen atom) bond, and the dangling bonds are used to form organometallic intermediates subsequently ending in C-C coupling by annealing to proper temperature as expressed in mechanism 2. The process of these two types of mechanisms is gradually conformed by STM, and plenty of efforts have been made to obtain large-scale, atomic precise and morphological diversified LD arrays on the substrate. The deep insight into the formation, mobility, and reaction of two typical mechanisms, which differ in the presence [68] or absence [69, 70] of organometallic intermediates as proposed by previous works at atomic-scale level, plays an important role in guiding the experiment in avoiding the effect from ambient factor.

Regarding Ullmann coupling, various reactive monomers, multiple functions of metal surfaces, relatively large discrepant activation temperature between the breaking of C-I bond and C-Br bond, and the combination with other types of synthetic reaction make the realization of polymers highly feasible. Choosing noble metal for Ullmann reaction is a distinctive characteristic. On the one hand, the noble metal used as substrate can strictly keep the certain dimension of chains and 2D arrays on the surface. On the other hand, different noble metal selected as catalysis would drive the process of reaction following these two different mechanisms. What is more, different kinds of precursors can trigger the coupling along the two different mechanisms under the same noble metal substrate, such as the coupling of tetraphenylporphyrins (TPP) with different numbers and

positions of peripheral Br atoms on Au(111) resulting in the formation of LD arrays, since no organometallic intermediates were observed [71]. However, the  $\text{I}_2\text{TMTP}$  (2',5'-diiodo 3,3'',5,5-tetramethyl-1,1':4',1''-terphenyl) on Au(111) resulted in  $\text{I}_2\text{TMTP}$  metal chain (as displayed in Figure 8) [14]. Actually on Au surface, not obtaining organometallic intermediates is a common phenomenon, and the generally accepted opinion is that the SSR are mobile, diffuse around on the surface of substrate, and form covalent bonds upon encounter. On the contrary, the organometallic intermediates with C-M-C bonds are constantly obtained on Cu [16, 72-74] and Ag surfaces [75, 76]. In a word, according to the explored experiments of Ullmann reaction, different experimental results can be briefly concluded in Table 1. Hence, the detailed atomistic knowledge of these processes is not very advanced, though the role of the different noble metal used for Ullmann coupling was discussed [72].

As an important aspect, organometallic intermediates formed on noble metal have the advantage that bond formation is reversible. Therefore, defects in the translational symmetry can be removed through bond scission and reformation [77]. Additionally, organometallic intermediates with thermally more stable structures than those based on the weaker electrostatic interactions or hydrogen bonds will enrich their potential applications in diverse fields. Because of the involvement of noble metal atoms, a versatile manner is possible for modulating the intrinsic electronic properties of organometallic nanostructures, such as organic superconductors [78]. From the sequence (g-i) in Figure 9 [77], the reversibility of organometallic intermediates is verified. While it is well known that metal surfaces are not static and that surface atoms can be extracted by adsorbates [79, 80], confirmation of organometallic intermediate in the Ullmann coupling would provide valuable insight into the reaction mechanism [81]. Therefore the reversibility might be a key factor contributing to getting relatively high-ordered nanostructures.

Compared to the polymers formed on Ag surface, the reason why the quality of ordered arrays on Cu surface is comparatively lower may be attributed to the irreversibility of the relatively strong C-Cu bonds [57]. The low ordered C-C coupled nanostructure is obtained from further annealing of organometallic intermediates. The halide ion (Br, I) from the cleavage of C-X (Br, I) adsorbed on the noble metal surface to hinder the process of polymerization. With increasing reactivity of the metal surface in the order  $\text{Au} > \text{Ag} > \text{Cu}$ , the activation barrier partly related to the relatively strong

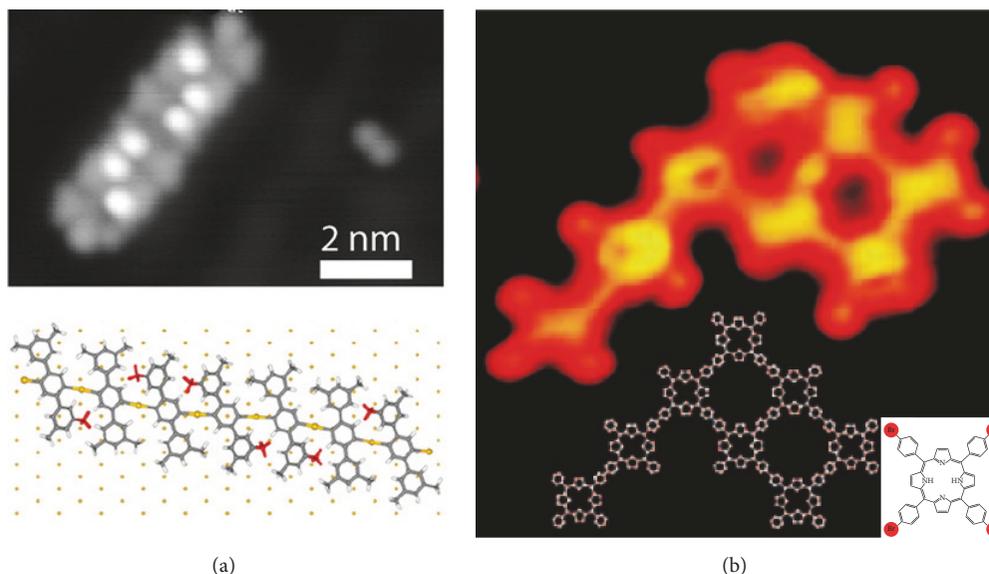


FIGURE 8: (a) STM image of self-assembled chains of TMTP monomers on Au (111) surface, with the molecular mechanics (MM) simulation of a linear TMTP chain. (b) STM image of direct C–C coupling between monomers. Figures are adopted from [14] with permission.

adsorption of the spit off halogens is likely to be different leading to the complexity of mobilizing halogens on the metal surface or desorbing from it. In the meantime, the dissociative negative halide ions gather together to hinder the coupling between monomers. Therefore, the interaction between halide ions and metal substrate directly influences the fabrication of organometallic intermediates or C–C bonded polymers. Often, these noble metal surfaces serve not only as platforms to impose 2D confinement but also as reactants that activate the molecules and participate in the reactions [16].

Apart from the effect caused by the catalyst of metal surface, the wide differences in activation temperatures for deiodination versus debromination on noble metal surface can be utilized for a defined sequential coupling depending on selective activation of iodine and bromine sites [15]. This novel way of sequential coupling through Ullmann reaction was applied on 5,15-bis(4'-bromophenyl)-10,20-bis(4'-iodophenyl)porphyrin (trans-Br<sub>2</sub>I<sub>2</sub>TPP) molecules leading to 2D nanoporous materials (Figure 1) [6]. In conclusion, the methodology of sequential coupling is realized by two typical ways: the reversibility of forming or detaching organometallic intermediates and vast differences in activation temperatures for deiodination versus debromination makes Ullmann reaction a popular bottom-up method to get large-scale crystalline nanostructure. But how to use the reversibility among the reaction in atomic precise level still needs more further explosion of the reaction to repair the defect and avoid the wrong coupling of C–C bond.

The imperfection inside low dimensional nanostructure may have relationships with many factors: deposition rate, annealing rate, surface temperature for direct polymerization, and direct versus hierarchical polymerization, besides a distinct surface influence result from noble metal surface and the diversity of monomers. Firstly, comparing Figures 9(a)–9(c),

the influence of deposition rate in direct polymerization was verified by a set of experiments where the deposition rates were varied over 2 orders of magnitude from  $<0.01$  to  $1.3 \text{ Hzs}^{-1}$  [15]. It is obvious that deposition with relatively high and intermediate rates leads to comparable network qualities with no statistically significant differences except extremely low rate ( $<0.01 \text{ Hzs}^{-1}$ ) ending in drastically impaired network (high probabilities of pentagonal and even tetragonal pores), so the situation occurs through hierarchical polymerization. Since surface temperature also has certain effect on the process of Ullmann coupling, two groups of experiments are taken into account: direct polymerization (Figures 9(e) and 9(f)) versus hierarchical polymerization (Figures 9(c) and 9(d)). In direct polymerization, polymerization at either lower or higher ( $375^\circ\text{C}$ ) temperature results in lower quality networks as compared to an intermediate temperature of  $250^\circ\text{C}$ , similar to hierarchical polymerization. Irregular pores are also crucial for hierarchical polymerization but less prior to thermal activation, corresponding to the difference between Figures 9(d) and 9(f).

As for hierarchical polymerization, the influence from surface temperature is fewer than that on direct polymerization. Additionally, the already polymerized 1D chains in first step that are subsequently interlinked into 2D networks appear to be a key in gradient for improving the structural quality, leading to the fact that direct polymerization exhibits a steeper temperature gradient than hierarchical polymerization [15]. For the effects as a result of surface temperature and deposition rates, on one hand, the limited lateral monomer mobility at lower temperatures and the presence of not fully activated iodine and bromine sites cause the large amount of open pores. Yet, higher temperatures similarly enhance the probabilities for irregular pores due to thermal agitation under 2D confinement for the backbone of monomers and low polymers. The reason stems from

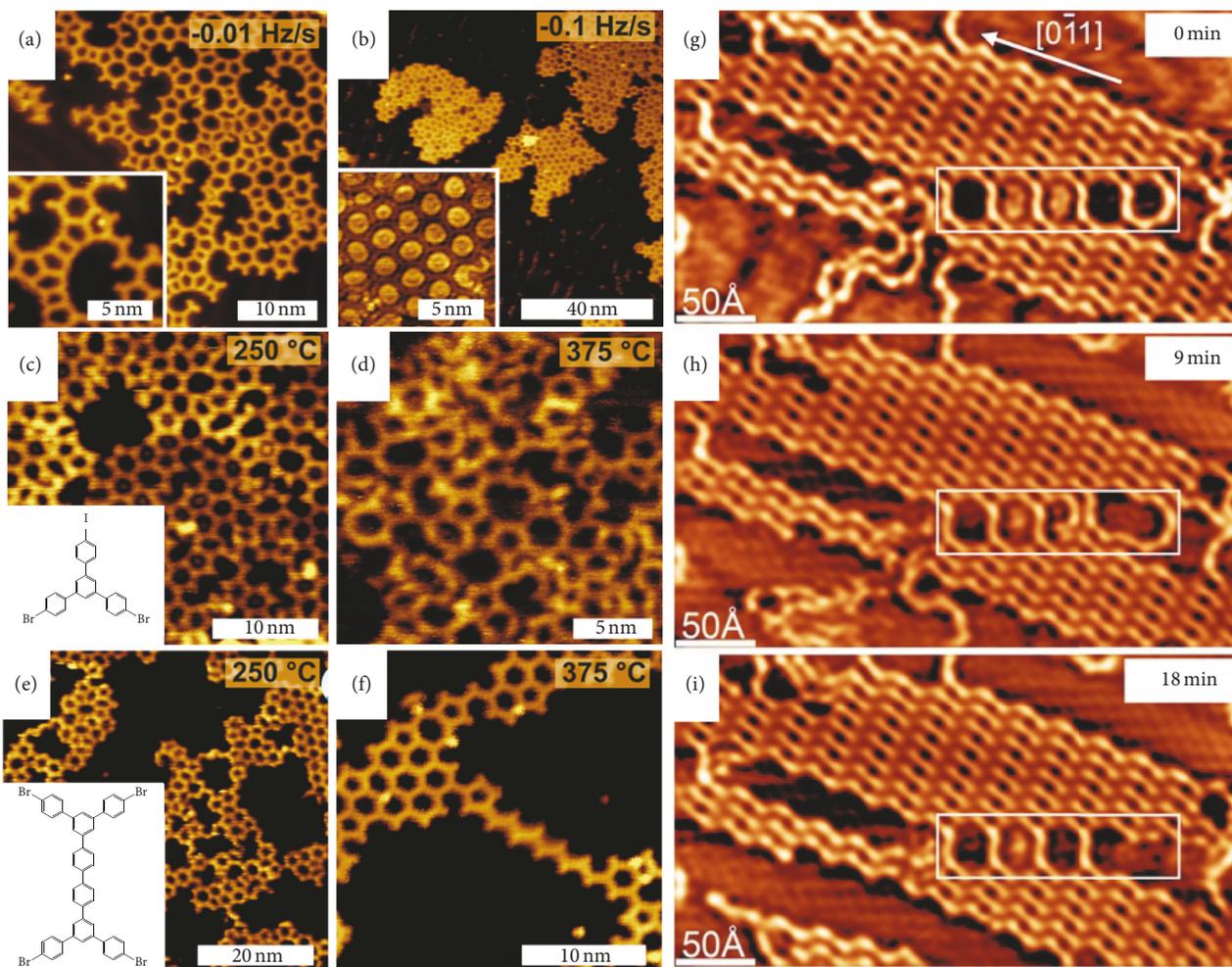


FIGURE 9: (a–d) STM images of covalent networks prepared by deposition of BIB onto Au(111) held at 250°C with varying rates corresponding to 0.01 Hzs<sup>-1</sup> (a), 0.1 Hzs<sup>-1</sup> (b), and 1.3 Hzs<sup>-1</sup> (c–d); images (c–d) vary in the substrate temperature for direct polymerization. Images (e–f) show thermal annealing was performed at different final temperatures of 250°C (e) and 375°C (f) for another molecule (TBQ) coupling to the polymers in the same deposition rate. The sequence (g–i) shows the dissociation and formation of C–Cu–C bonds. Figures are taken from [15] with permission.

two aspects: (1) excessively high temperatures cause C–C linkage deviating from their ideal positions through bending of C–C  $\sigma$  bonds [82]; (2) unimolecular reaction is associated with a notable activation barrier which is larger than the bimolecular reaction, hence becoming favored at higher temperatures [15].

Through the analysis of a series of factors related to the experiment of Ullmann reaction, the structural quality of covalent networks obtained by kinetically controlled coupling reactions can be improved by optimization of reaction parameters. Surely vacancy defects can be compensated by sequential precursor deposition, since the subsequently dosed precursors can fill the vacancies and are afterwards being hindered from diffusing across domain boundaries [82]. However, the improvement in the quality of polymers is limited. Firstly, more further insight into the noble metal surface is necessary for taking advantage of the reversibility of organometallic intermediates in high precision to correct the deformation and defect. Then it is verified that Br

atoms are tightly bound to the metal surface or intermediate polymer chains [83] resulting in the preparation of the long-range ordered LD nanostructure being hindered. On the other side, the UHV condition is relatively expensive for fabricating the LD materials. In summary, many fancy LD nanostructures [84] have been discovered depending on Ullmann reaction which makes it a popular bottom-up synthetic method, though there is still further optimization to avoid the deformation of C–C coupling and even the reversibility of C–C bonds in control.

*2.5. Optimization of Hierarchical Polymerization Combined with Ullmann Reaction.* To date, the methodology of the bottom-up synthetic method depending on Ullmann coupling has been well-developed. However, it is hard to gain novel achievement or make a big breakthrough in applying into product just by one independent polymerization. Nowadays some interesting schemes related to the combination of Ullmann reaction with other types of polymerizations such

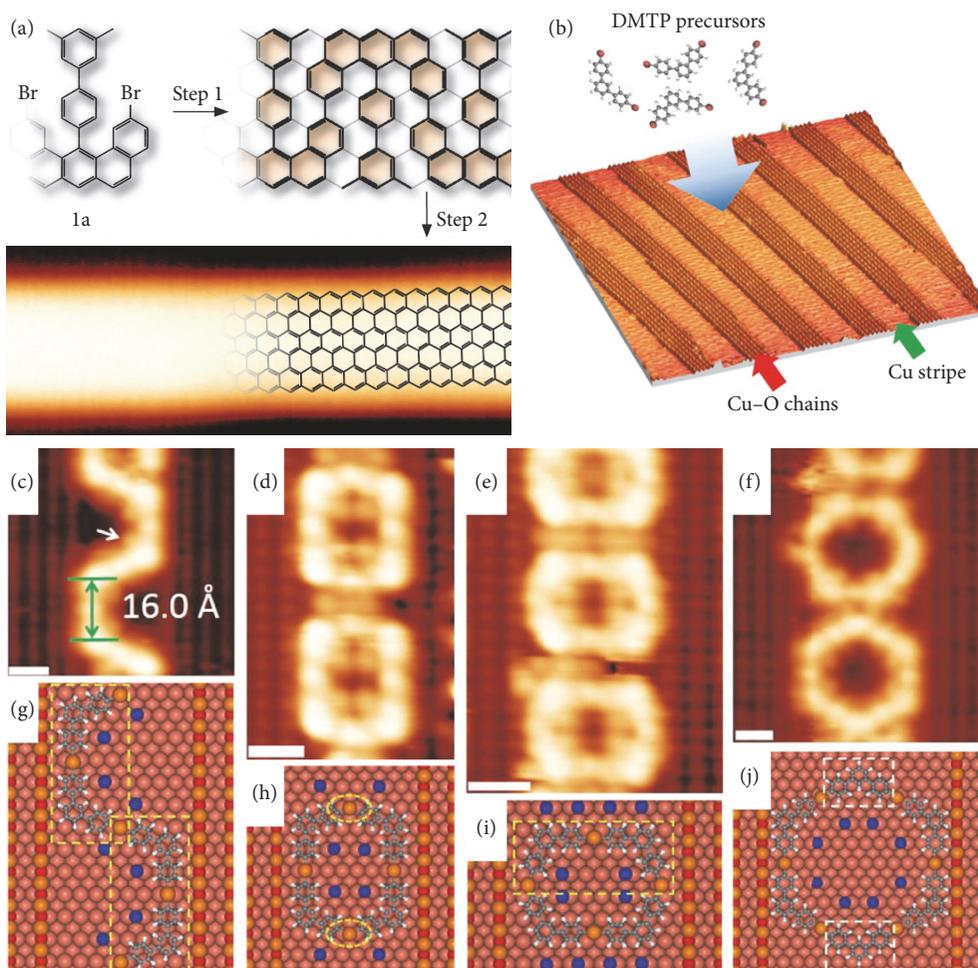


FIGURE 10: (a) Monomer with an additional dimethyl-biphenyl group in the interior of the U-shape to afford a 6-ZGNR upon polymerization (Step 1) and subsequent cyclization (Step 2). STM image of the Au (111) surface after annealing at 625 K indicates the complete cyclodehydrogenation of the polymers and the formation of 6-ZGNRs. (b) The scheme of Ullmann coupling with the monomers DMTP performed on the interesting template Cu(110)-(2 × 1)O nanotemplate is expressed, and the STM images (c–f) show the magnified view of organometallic species formed on the sample in panel depending on different reaction pathways tuned by the different widths of bare Cu stripes on a Cu(110)-(2 × 1)O surface. The corresponding molecular models are shown in (g–j). Images are taken from [16] with permission.

as cyclodehydrogenation reaction [85], lithography [16], and boronic acid polycondensation [54] were performed not long ago. Among them, the most typical one is the hierarchical polymerization that begins with the bottom-up synthetic Ullmann coupling and ends in cyclodehydrogenation reaction. As the protocol showed in Figure 10(a), atomically precise zigzag edges are yielded through the bottom-up synthesis of zigzag GNR through surface-assisted polymerization and subsequently cyclodehydrogenation of specifically designed precursor monomers. The first step of the scheme, Ullmann coupling, lays the foundation of the whole structure of nanostructure. And then cyclodehydrogenation causes the particular sites C coupling to the other C end in a C-based hexatomic ring. The dehydrogenation needs further annealing to activate the C–H bond. Hence this type of sequential activation selectively couples adjacent C with H<sub>2</sub> molecules separated due to Ullmann coupling creating a dynamite position of C atoms. A set of GNR with the diversity

of topological edge [74, 86–88] or different sized porous nanosheets have been fabricated leading to the opening of substantial electronic band gaps that are directly linked to their structural boundary conditions [89].

Another novel hierarchical polymerization is the lithography followed by Ullmann coupling in mechanism 2 to realize high degree of structural controlled synthesis of organometallic chains and macrocycles by employing a Cu(110)-(2 × 1) nanotemplate [16]. It is an interesting scheme to start the control of the polymerization from the metal surface to confine the low dimensional nanostructures located in a regular position. The polymerization of monomers 4,4''-dibromo-metaterphenyl (DMTP) on a Cu(110)-(2 × 1)O surface has several reaction pathways leading to different widths of the organometallic polymers adsorbed on the metal surface. Hence it is a creation of this hierarchical polymerization that realizes the selection of the pathway of Ullmann reaction depending on the width of metal stripe.

There is no doubt that hierarchical polymerization centering on Ullmann coupling serves as the optimized polymerization improving the will of controlling the fabrication of low dimensional nanomaterials.

### 3. Conclusions and Perspectives

Tremendous progress has been made in surface-assisted synthetic science as a consequence of breakthroughs in synthetic strategies and methods benefited from advancement in the mechanism insight in theory and rapid development of instruments and techniques. This paper has reviewed the widely utilized bottom-up coupling methods for fabricating low dimensional nanostructures via phase transforming. Taking into account the seriously limited solubility of large molecules and the uncertainty of applicability of aggregates for solution chemistry into surface chemistry, on-surface polymerization has already demonstrated its promising potential as a facile bottom-up approach in atomic precise level and better confined the polymers on the 2D platform. What is more, the on-surface polymerization possesses its special advantages which make it popular in nanoscience; for instance, dehydrogenative coupling has abundant coupling sites to realize the diversity of the polymers and the H<sub>2</sub> byproduct can be easily desorbed from the surface. In fact, nowadays surface-assisted reactions of large aromatic molecules on single-crystal metal surfaces can be considered as a workshop in which surface physics, catalysis, organic chemistry, and nanotechnology get together to test fundamentally new ideas about on-surface chemistry. From this point of view, the advantages, mechanism of the interaction between adsorbed monomers and substrate, characteristics of polymers, influence related to the reaction, and the disadvantages are deeply discussed. Besides the mentioned surface-assisted coupling reactions, other reactions such as dehydration reaction, click reactions [90], have also been developed in polymerization.

Dating back to synthetic reactions firstly transferred to solid surface under the ambient environment or UHV conditions, the insight of the reaction in theory has been continuing while experimental techniques keep being improved, diverse kinds of low dimensional nanostructures have been fabricated, and the quality of nanostructure has been greatly improved. Meanwhile, dynamic mechanism of whole reaction systems has also been explored deeply by DFT theory, including the phase transforming during reaction [28, 91]. However, side-reactions still exist for surface-assisted coupling; topological defects remain the most severe issue. Even though the interesting characteristics, for example, the reversibility of the polymerization, have been discovered, there is still no good scheme to take advantage of it so that the deformation of the polymers can be corrected. In addition, the halogen atoms spilt from monomers in the process of Ullmann reaction are still a serious problem that hinders the long-range ordered nanostructure formed on the metal surface. Additionally, thermally activated side reaction pathway or agitation of carbon skeletons also needs to be avoided after further optimization.

In short, the surface-assisted bottom-up coupling reaction opens up a door to the next generation low dimensional nanomaterials. Although there are still many problems that need to be overcome, a set of novel schemes, like the hierarchical polymerization owing to the advantages of many other types of coupling reactions, make it possible to deal with the challenges we are facing now. In a word, on-surface chemistry remains far from being predictable. According to the paradigm theory in condensed matter physics, the emerging hierarchical polymerization, similar to the coupling of DMTP on Cu(110)-(2 × 1)-O nanotemplate, can give us inspiration to fabricate novel low dimensional nanostructures, such as organometallic nanowires with controllable phase transformation.

### Conflicts of Interest

The authors declare that they have no conflicts of interest.

### Acknowledgments

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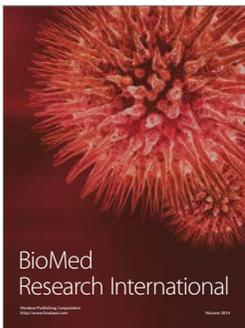
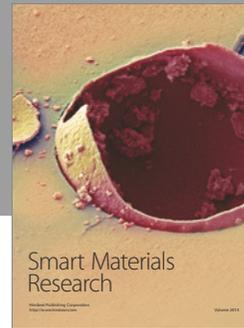
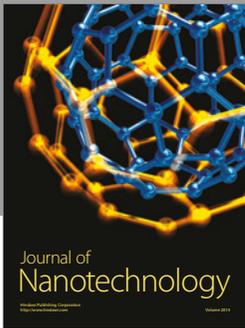
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