Reviews

Two-Dimensional Polymerization and Reaction at the Solid/Liquid Interface: Scanning Tunneling Microscopy Study

Rusong XIE,* Yonghai SONG,* Lingli WAN,* Huizhen YUAN,* Pengcheng LI,* Xianping XIAO,* Li LIU,* Shuhong YE,* Shengbin LEI,† and Li WANG*†**

**College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, P. R. China*
***Key Laboratory of Microsystems and Microstructures Manufacturing, Ministry of Education & The Academy of Fundamental and Interdisciplinary Science, Harbin Institute of Technology, Harbin 150080, P. R. China*

The two-dimensional polymerization and reaction at the solid/liquid interface has caused considerable attention in recent years because of its fundamental importance and many potential applications. Scanning tunneling microscopy (STM) provides the possibility for the observation and manipulation of polymerization and reaction occurring at the solid/liquid interface at the atomic level. Two-dimensional polymerization and reaction could be induced by external stimuli, such as electrochemistry-induced, STM tip-induced, or light-induced. The polymerization at the solid/liquid interface is the focus of this review, including the mechanism of polymerization and characterization of structural and electrical properties of the resulting polymers. Finally, the outlooks for developments in this field are described.

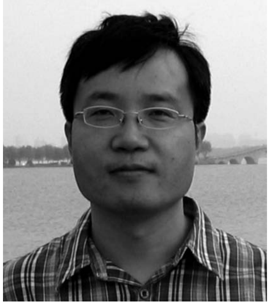
(Received September 18, 2010; Accepted November 30, 2010; Published February 10, 2011)

1 Introduction

Solid/liquid interfaces are peculiar, but exist universally in nature and in biosystems. Reconstruction will occur in an electrode surface when it is dipped into a solution and forms a solid/liquid interface. The solid/liquid interface provides the particular environment to implement the self-assembled polymerization, which can be observed by scanning tunneling microscopy (STM).

The STM is a powerful technique to observe structures and reactions or to manipulate molecules, atoms and reactions at the solid/liquid interface.[1,2] With the help of STM, a variety of achievements were achieved in the surface and interface science.[3-28] Based on the quantum tunneling effect, the information of the surface or interface can be revealed by the change of tunneling current in the real space.

Two-dimensional (2D) supramolecular polymers can form on the solid/liquid interface through noncovalent interactions and 2D polymers can also form on the solid/liquid interface through covalent interactions. In recent years, 2D polymerization at the solid/liquid interface has attracted more and more interest



Shengbin LEI obtained his PhD in 2002 in physical chemistry at the Institute of Chemistry, CAS (China) with Prof. Chen Wang. After working for four years at the same institute in the field of surface assembly, he joined the group of Prof. Steven De Feyter at K. U. Leuven in 2006, and worked in the field of 2D nanoporous networks and host-guest chemistry. He joined HIT in Sept. 2009 as a professor. His current research focuses on 2D crystal engineering at the interfaces and the characterization of nanomaterials.

Li WANG obtained her PhD in 2003 in analytical chemistry at the Changchun Institute of Applied Chemistry, CAS (China) with Prof. Erkang Wang. She then joined the group of Prof. Kingo Itaya at Tohoku University and worked in the field of constructing molecular nanostructures and nanoporous networks for two years. After that she joined Jiangxi Normal University in Jul. 2006 as a professor. Her current research focuses on the design and characterization of nanostructures at surfaces/interfaces.

---

† To whom correspondence should be addressed.
E-mail: lwang@jxnu.edu.cn; leisb@hit.edu.cn

because it can produce 2D polymers with single molecule thinness. The conjugated polymers are widely used as active materials in field effect transistors (FETs),[29] light-emitting diodes (LEDs),[30,31] and photovoltaic cells.[32-34] The STM investigations of the polymerization and reaction at the solid/liquid interface not only reveal atomic details of reaction mechanisms but are also relevant for potential applications such as surface functionalization and patterning, nanoreactors and switches.

Herein, we review some methods of polymerization at the solid/liquid interface in recent years starting with a brief introduction to the STM technique and the solid/liquid interface. Electrochemistry-induced polymerization is a frequently used technique in the formation of 2D polymers. By using the molecule-molecule, molecule-surface interactions and the electrical excitation, one can stimulate the 2D polymerization. Utilizing STM tip to induce the polymerization reaction has also been reviewed. In addition, controlling the applied potential between the tip and surface, some surface defects can be formed, which are able to control the polymerization process. Photo-irradiation is usually used in the organic reaction, so introducing the photo-irradiation into 2D polymerization at the solid/liquid interface may be an effective way. Beside these methods, scientists are also searching for other ways in recent years, these will also be introduced in this review.

2 STM Introduction

Scanning tunneling microscopy (STM) was invented by Binnig and Rohrer in 1982.[1,2] Because of its great impact on surface science and engineering science, these two scientists quickly shared the Nobel Prize for Physics with Ruth Card in 1986. There are many features of STM, such as high-resolution, real-time and real-space to obtain the information about 2D surfaces. It can work under ultrahigh vacuum (UHV), ambient and even aqueous solution conditions. In combination with other analytical techniques, the information about surface electrical structure and composition can be gained. It provides the first time that human beings can observe the arrangement of single atoms and physical/chemical properties of surfaces at the atomic level. At the same time, it is also the first time we can manipulate the atoms, molecules and reactions on the surface. The emergence of STM has a great impact in nanochemistry, surface chemistry and material science.

STM is based on the quantum tunneling effect to image the sample surface. There are several STM modes, for instance, electrochemical scanning tunneling microscopy (ECSTM), ultrahigh-vacuum scanning tunneling microscopy (UHV-STM) and normal STM. The difference between ECSTM and normal STM is that ECSTM has a potentiostat to control the electrochemical experiment when it is imaging. The electrochemical cell is composed of four electrodes including two work electrodes (WE) (namely, the STM tip and the sample substrate), one reference electrode (RE) and one counter electrode (CE).

STM usually has two operation modes: constant height mode and constant current mode. In the constant height mode, the height between the tip and the sample surface is constant during raster scanning, and the tunneling current is changing all the time. Oppositely, in the constant current mode, the current between tip and surface is kept constant and the height information is recorded. And then through the software manipulation, the topography and electronic information about the sample surface is obtained.

3 Solid/Liquid Interface

It is of great importance to understand the formation of highly ordered molecule monolayers at the solid/liquid interface, because of its relevance both in the theoretical and practical aspects, such as molecular recognition between proteins,[35] crystallization[36] and chemical reactions.[37] Solid/liquid interfaces have attracted the attention of scientists from various fields, such as chemists, metallurgists, biologists, physicists and engineers, because of its surface constitution, surface-structure sensitive properties and the great variety of phenomena occurring at solid/liquid interfaces.[38] After Helmholtz proposed a model of the electrical double layer and realized the importance of the electrical nature of the solid surface in contact with the electrolyte solution in 1879, Parsons further developed the study by considering the distribution of ions and solvent molecules in the double-layer in 1954.[39-43] The double layer consists of the inner layer and the outer layer. On the metal surface and thin layer of solution near the surface of metal, the equal quantity of cations' and anions' surplus charge forms the double layer.

Now, with the development of science and technology, many unique features were revealed by the STM images of the solid/liquid interface. Reconstruction will take place at the solid/liquid interface when some electrodes are dipped into a solution. The reconstructed surface has a new surface structure different from an ideal crystal surface.[44] There are many kinds of electrodes such as Au,[45,46] Cu,[47-49] Pt,[50-52] Si[53] which can generate the reconstruction by using different methods. These methods resulted in the electrode reconstruction at the solid/liquid interface are mainly classified into three aspects: the thermal-induced reconstruction, the potential-induced reconstruction and the absorption-induced reconstruction. The usual reconstruction of the Au(111) surface induced by the applied potential is shown in Fig. 1. The reconstructed surface becomes the (fcc)-(bridge)-(hcp)-(bridge)-(fcc) domains with different surface heights.[45] Along the <110> direction of the reconstruction, 23 atoms are compressed and occupied 22 atomic positions, which also lead to the change of the height of the electron. The Au(111) single crystal structure changes from Au(111)-(1×1) to Au(111)-$(22 \times \sqrt{3})$ and the atomic structure of the solid/liquid interface is also different.

Beside the self-assembly under the UHV conditions, the solid/liquid interface has its own unique advantages.[15,54-57] First, the solid/liquid interface is easily obtained, and does not need a complicated or expensive infrastructure. Second, many organismal macromolecules can not be gasificated under UHV conditions and almost all enzymes degenerate in high temperature; thus, the solid/liquid interface provides the possibility for the self-assembly of organismal macromolecules. Third, the solvent has a great influence on the system, which makes it possible to tune the assembling structure by adjusting the properties of solvents. Last, the dynamic nature of solid/liquid interface allows repairing of defects in the self-assembled layers (self-healing) by the dynamic exchange of molecules adsorbed on the surface and in the liquid. With all these advantages, self-assembly at the solid/liquid interface attracts more and more interest of scientists.

With the help of STM, we can directly observe the surface reconstruction at solid/liquid interface at the atomic level.[58] Thus STM is a pragmatic tool for visualization at the atomic level, and it can also be used as a manipulating tool in the molecular engineering and nanoscience.

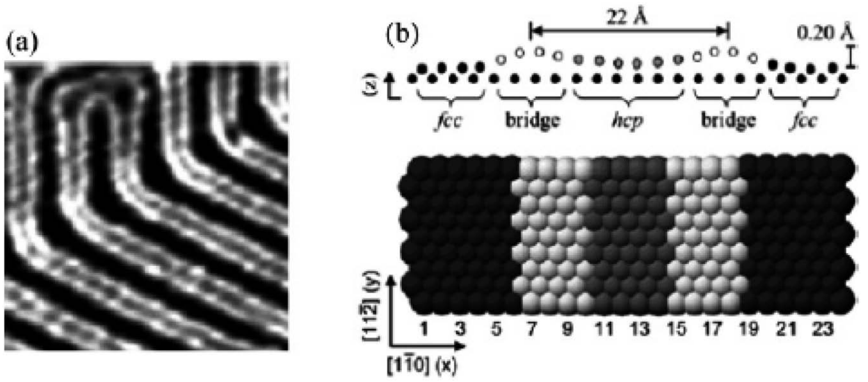


Fig. 1 STM image (a) and its structural model (b) of Au(111)-$(22\times\sqrt{3})$ reconstruction (Adapted with permission from Ref. 45. Copyright American Chemical Society).

4 Tip-Induced 2D Polymerization

STM is a pragmatic methodology to probe the structure and the properties of physisorption/chemisorption at the atomic level. At the same time, it is also an effective tool in handling atoms, molecules and reactions on a surface. The controllable manipulation includes lateral movement, vertical transfer, and dissociation of single molecules on a surface.[59-68] Now, using an STM tip to initiate and control the polymerization or reaction at the solid/liquid interface is an interesting topic.[69-71]

Because of the excellent conductive properties, poly-diacetylene (poly-DA) and its derivatives are widely used in chemosensors, composite materials and biomimetic materials. The polymerization of diacetylene (DA) can be stimulated by the STM tip. Many groups including Nishio[72] and Sullivan[73] *et al.* have studied its polymerizations at the solid/liquid interface by tip-induced methods. Takajo and coworkers[69] used a tip-induced method to control the chain polymerization of 10,12-nonacosadiynoic acid ($CH_3(CH_2)_{15}$-C≡C-C≡C-$(CH_2)_8COOH$) on a highly oriented pyrolytic graphite (HOPG) substrate. It was found that two triple bonds of the 10,12-nonacosadiynoic acid molecules could be broken and would form a new double bond. This is the foundation of the polymerization of diacetylene compounds.[74,70,71] Figure 2 is the typical STM image of 10,12-nonacosadiynoic acid adlayers with a poly-DA nanowire indicated by a very bright line. The polymerization was found to occur on a step edge of the topmost layer. These authors attributed the polymerization to the multiple vibrations which led to repetitive collisions with charged carriers, initiating diacetylene (DA) polymerization at the solid/liquid interface. Takajo and coworkers suggested that the inelastic energy transformation of the tunneling electrons resulted in the electronic excitation of DA moieties and simultaneously began to polymerize. With an applied pulse potential between the STM tip and the HOPG substrate, the polymerization of DA moieties has been carried out. This method may be widely used in the self-assembled molecules at solid/liquid interface to form an ordered 2D polymer with single molecule thickness.

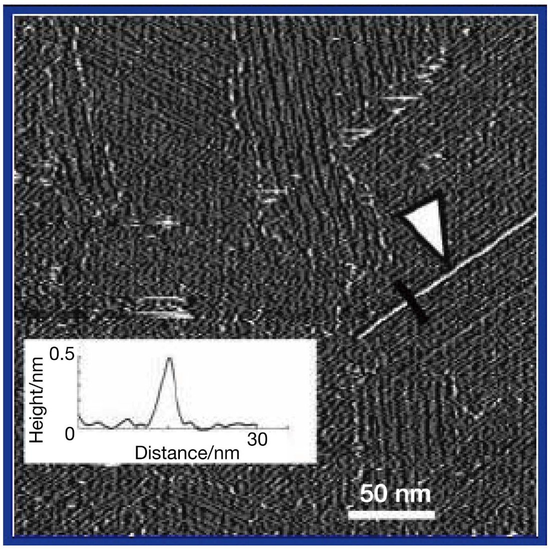


Fig. 2 STM image of the first 10,12-nonacosadiynoic acid layer on HOPG obtained at 8 min after dropping the DA solution. A pulsed sample bias (–4 V high, 5 μs wide) was applied to an array of DA moieties indicated by the white arrow. A poly-DA nanowire indicated by a very bright line can be seen. The inset shows a section profile across poly-DA (Reprinted with permission from Ref. 69. Copyright American Chemical Society).

Okawa and his coworkers also studied the manipulation of polymerization of 10,12-nonacosadiynoic acid molecule with the tip-induced method.[75] At first, a 6-nm-wide hole as an artificial defect was created in the monolayer, where the position was preset by the STM tip with a positively pulsed sample bias (~5 V in height, 10 ms in width). After the defect was created, it was time to polymerize. The STM tip was gliding from top to bottom (Fig. 3) and a negative pulse (14 V, 5 ms) was applied at the site indicated by arrow 1. The chain polymerization started at this point and terminated when it met the defect. Between the initial position of tip and the artificial defect, a bright line was observed. With the help of structural analysis, it has been proved that this is a polymerized poly-DA nanowire (Fig. 3).

The STM tip not only can induce the polymerization reaction, but also can control all steps of a chemical reaction. Hla *et al.* studied the Ullmann reaction steps by STM on the Cu surface.[76,77] The synthesis reaction of biphenyl from iodobenzene include three steps: (a) dissociation of iodobenzene (C_6H_5I) into phenyl (C_6H_5) and iodine; (b) diffusion of phenyl to find another phenyl as a reaction partner; (c) association to form biphenyl ($C_{12}H_{10}$). Figure 4 is a typical schematic image of all the steps of this Ullmann reaction. Firstly, the STM tip induces dissociation of iodobenzene (C_6H_5I) into phenyl (C_6H_5) and iodine. Then the iodine is moved aside along the step edges by the STM tip. One phenyl (C_6H_5) shifts to the neighboring phenyl (C_6H_5) in order

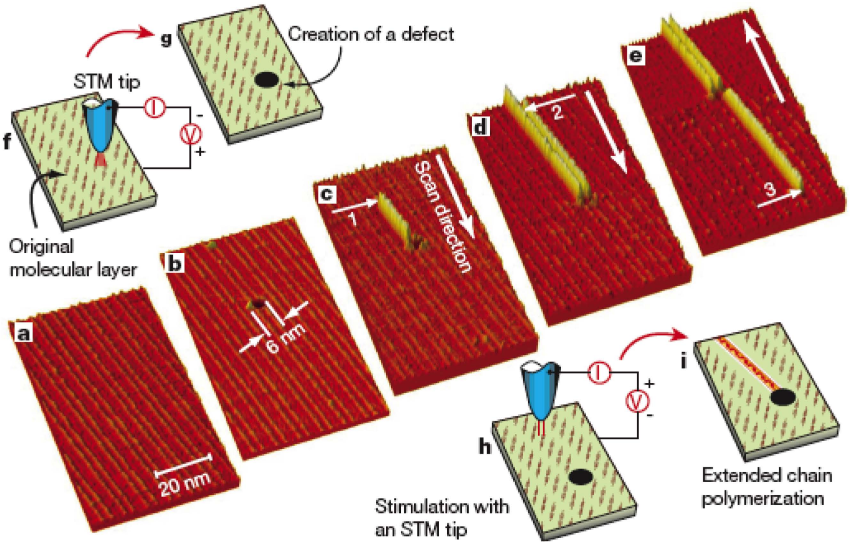


Fig. 3 STM images and diagrams showing the process of controlling the initiation and termination of linear chain polymerization with an STM tip. STM images were obtained in air at room temperature in constant-current mode. a, STM image of the original monomolecular layer of 10,12-nonacosadiynoic acid. b, Creation of an artificial defect in advance in the monomolecular layer using an STM tip. c, First chain polymerization, initiated at the point indicated by arrow (1) using an STM tip, and terminated at the artificial defect. d, Second chain polymerization, initiated at arrow (2). e, Third chain polymerization, initiated at arrow (3). f, g, Creation of an artificial defect in advance with an STM tip. h, i, Initiation of chain polymerization with an STM tip, and termination of the polymerization at the artificial defect (Reprinted with permission from Ref. 75. Copyright Nature).

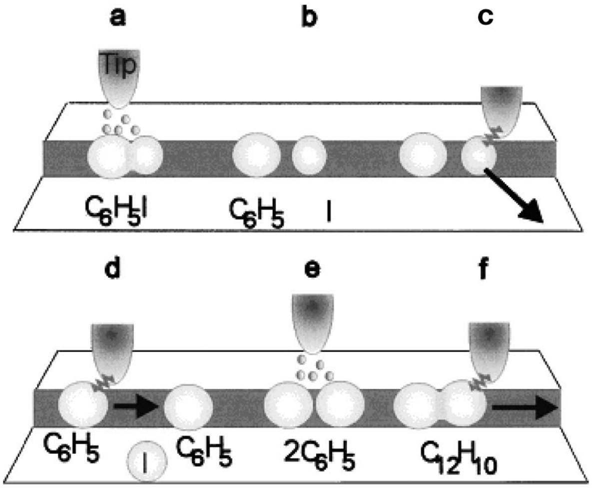


Fig. 4 Schematic illustration of the STM tip-induced synthesis steps of a biphenyl molecule. (a) and (b) Electron-induced selective abstraction of iodine from iodobenzene. (c) Removal of the iodine atom to a terrace site by lateral manipulation. (d) Bringing together two phenyls by lateral manipulation. (e) Electron-induced chemical association of the phenyl couple to biphenyl. (f) Pulling the synthesized molecule by its front end with the STM tip to confirm the association (Reprinted with permission from Ref. 77. Copyright American Physical Society).

to prepare the conjugation reaction. At last, through the applied potential between the tip and the Cu surface, the conjugation reaction is completed and forms biphenyl ($C_{12}H_{10}$). So with the help of the STM tip, all steps of Ullmann reaction can be reviewed clearly.

The STM tip-induced polymerizations give us an original idea on the fabrication of novel molecular nanoelectronic devices and suggest various new types of physical and chemical experiments on the nanoscale.

5 Light-Induced 2D Polymerization

Light irradiation is also a useful method in initiating the polymerization. With the photo-irradiation, some polymerization reactions will be carried out or changed. The light-driven polymerization was investigated by De Feyter and De Schryver.[78-80] The monolayer of a terephthalic acid derivative consisting of two diacetylene chains was prepared by the Langmuir–Blodgett technique with horizontal lifting method and irradiated for 30 min with UV light. From Fig. 5A, we could observe three bright lines with the same orientation in one domain, and these bright lines were considered as polymerized diacetylene rows. UV irradiation led to the initial random polymerization, and then when a potential pulse was applied through the STM tip, a new polymerized diacetylene backbone emerged (Fig. 5B). The reason for the low probability of polymerization was attributed to the substrate and/or the nonoptimal orientation of the diacetylene units. Here, Fig. 5C is a typical molecular model of a 2D nanostructure formed by the covalent connection of adjacent parallel polydiacetylene chains. This study demonstrated the possibility of forming 2D polymers by light-induced 2D polymerization.

Some bulk polymerization reactions are based on the surrounding excitation, such as light irradiation and thermo-induced polymerization. The reactions at the solid/liquid interface are also influenced by these factors.[78] Takami and coworkers studied the photopolymerization of 1,15,17,31-dotriacontatetrayne (DTTY) molecules which formed a cloth-like macromolecule (atomic cloth) on the graphite surface.[81] 1,15,17,31-dotriacontatetrayne (DTTY) molecules consist of acetylene and diacetylene; these two parts can form flat lying alkyl chains which cross-linked alternately by polydiacetylene (PD) and polyacetylene (PA) chains. Because of the PD and PA are both conjugated compounds, polyDTTY has the long conjugated systems. Figure 6a is the schematic drawing of the formation of the polyDTTY. Figure 6b is a typical STM image of the polyDTTY after the UV irradiation, the orientated domain was found on the graphite surface which covered the surface with the flat lying alkyl chains. Based on the analysis of Fourier transformation of STM images, the authors concluded that the atomic cloth was not commensurate with graphite in all directions, most probably point-on-point coincident in one direction and point-on-line in another direction.

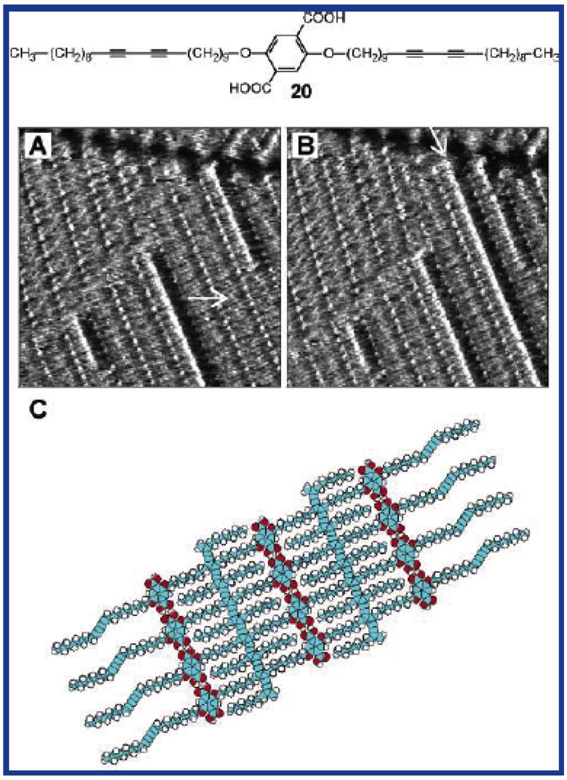


Fig. 5 (A) STM image of a monolayer of 2,5-(10,12-henicosadiynyloxy) terephthalic acid (TTA-DIA) after 30 min of UV light irradiation. A pulse (height, –3.2 V; width, 500 ns) was applied at the position indicated with a white arrow. (B) STM image of the monolayer of TTA-DIA at the same area after application of a single pulse. The white arrow in the image indicates the polydiacetylene backbone created by pulsing. Scanning conditions for both A and B were identical. Image size: 27.1×27.1 nm^2. $I_{\mathrm{set}} = 0.40$ nA, $V_{\mathrm{bias}} = -0.40$ V. (C) Molecular model of a 2D nanostructure formed by the covalent connection of adjacent parallel polydiacetylene chains (Reprinted with permission from Ref. 80. Copyright American Chemical Society).

6 Electrochemistry-Induced 2D Polymerization

In recent years, using organic monomers to form 2D structure at solid/liquid interface by electrochemical methods has attracted more and more attention.[82-99] These monomers included thiophene,[82] aniline,[83] nitrobenzene[85] and other molecules.[100-111] Many noble metals such as Au(111), Cu(111) and Ag(100) were frequently used as substrates. *In situ* STM provides a novel way to directly observe the processes of the polymerization at atomic level.[112]

Polyaniline (PAN) molecules had been reported to adsorb on Au(111) surfaces and could be observed by *in situ* STM.[83,84,90-92] In the 20th century, PAN had been investigated widely in electrochemistry and material science[93-95] because of its potential applications, such as fabricating sensors, batteries, light-emitting devices, and electrochromic devices.[96-99] The polymerization of aniline on Au(111) was carried out in the mixed solutions of an inorganic acid and aniline. The ordinary inorganic acids are sulfuric acid, hydrochloric acid, nitric acid and perchloric acid, and the rate of polymerization in the different inorganic acids diminishes in the sequence of $HClO_4 < HNO_3 \approx HCl < H_2SO_4$. This is because the anions play an important role in the polymerization of aniline. On the one hand, anions can form ion-pairs with aniline. On the other hand anions have an impact on the oxidation and reaction of aniline and PAN molecules. Ou Yang and coworkers directly visualized aniline admolecule and its electropolymerization on Au(111) with *in situ* STM.[83] The oxidative polymerization of aniline would occur if the potential $E > 1.0$ V. Long-range ordered adlattices were readily discriminated amid randomly distributed islands. Adsorption of aniline monomers led to the ordered arrays and the protruded islands which were raised by 0.25 nm above the terrace were aggregated gold adatoms injected from the Au(111) surface

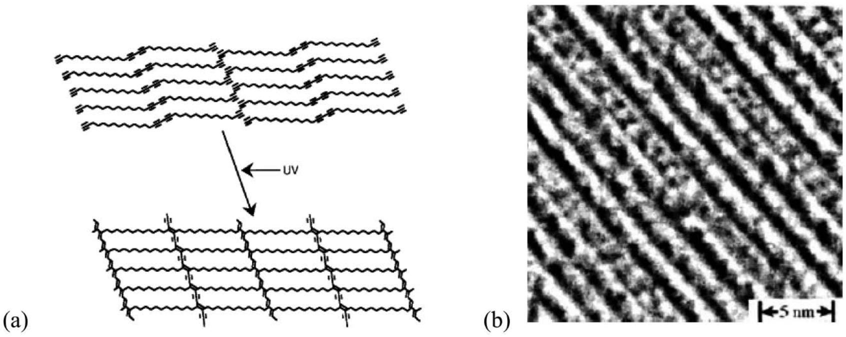


Fig. 6 (a) Schematic drawing of the atomic cloth prepared by photopolymerization of DTTY molecules that were laid flat and closely packed in a monolayer; (b) UHV-STM image of the atomic cloth on graphite surface. Sample bias, +0.2 V; tunneling current, 0.1 nA; image sizes, 20.0×20.0 nm^{-2} (Reprinted with permission from Ref. 81. Copyright Wiley-VCH).

upon the lift of reconstruction. The polymerization of aniline could be initiated by exerting a pulse potential at the interface. Figure 7a shows an ordered array of aniline on the Au(111) surface at 0.9 V. Under this potential, aniline did not polymerize. Until the potential value was increased to 1.05 V (Fig. 7b), aniline began to polymerize. The polymer line preferentially grew along the <121> direction of the Au(111) surface. From Fig. 7c we could observe that with the time increasing the line of the PAN became longer and inevitably deformed. Figure 7d is a typical further high-resolution STM image of the PAN molecule and reveals the internal molecular structure. All the brighter stripes were the PAN molecules, and the bright spots in the stripes were attributed to the phenyl rings of anilines. The distances between neighboring phenyl rings inside one PAN chain indicated that aniline conjugated in a head-to-tail manner in PAN.

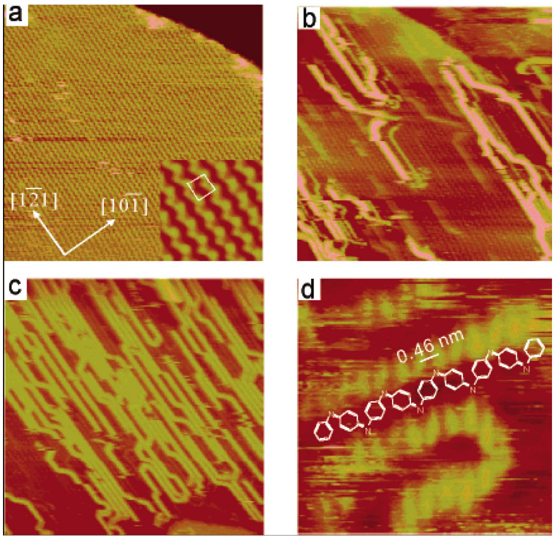


Fig. 7 Time-dependent *in-situ* STM images recorded on Au(111) at 0.9 V (a), and 1.05 V (b – c). The images in panels b and c were collected at 1 and 20 min after the shift of potential from 0.9 to 1.05 V. Scan areas (a – c) are 50 × 50 nm^2 and (d) 6 × 6 nm^2 (Reprinted with permission from Ref. 83. Copyright American Chemical Society).

The different conformations of aniline in the polymerization process at different potentials were also investigated by the *in-situ* STM.[86] It was found that aniline admolecules which adsorbed on a well-ordered Au(111)-(22 × $\sqrt{3}$) reconstructed surface at 0.8 V could be easily oxidized and transformed into a well-defined PAN with linear molecular conformation if the potential value exceed 0.95 V. X-ray photoelectron spectroscopy (XPS) and near edge X-ray absorption fine structure (NEXAFS) results indicated that these linear PAN molecules assumed an emeraldine salt form made of PAN chains and (bi) sulfate anions. When the potential was changed between 1.0 and 0.5 V, the conformations of the emeraldine salt of PAN could be alternated from straight to crooked. This was attributed to the restructuring of the Au(111) electrified interface. At $E > 0.95$ V, the coadsorbed bisulfate anions that serve as anchors to immobilize the PAN chains were desorbed when the potential switched negatively, which results in the twist of PAN chains. The adsorption/desorption of bisulfate anions and PAN molecules and the restructure of the electrified interface of PAN on Au(111) were determined by the change of applied potential.

Polythiophene and its derivatives are another kind of conducting polymers (CPs) which has become a focus in the materials science, nanoscience and engineering. Using

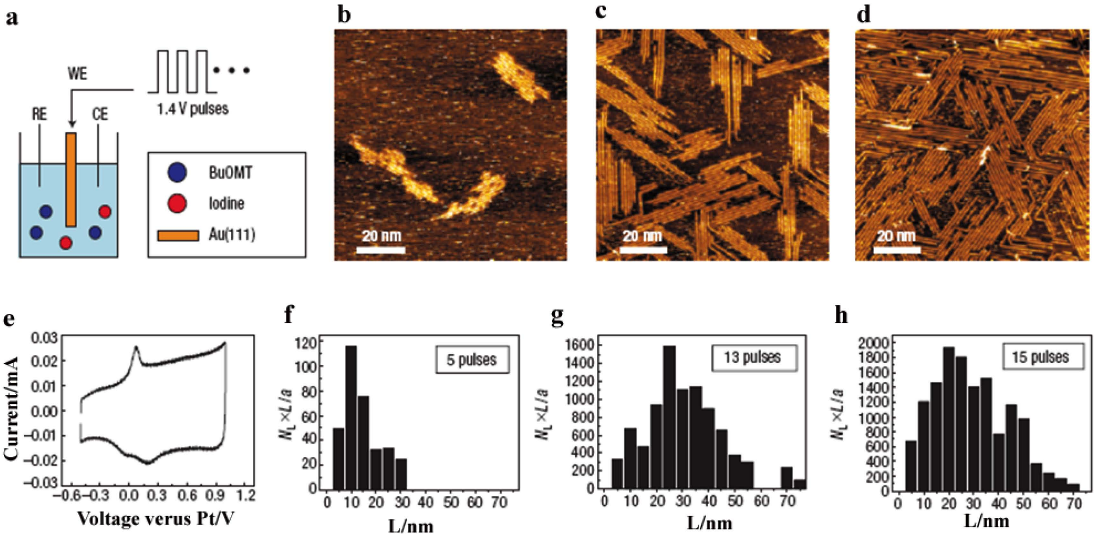


Fig. 8 Electrochemical epitaxial polymerization of single-polythiophene wires. a, Experimental set-up of electrochemical epitaxial polymerization. WE, RE and CE denote working, reference and counter electrodes, respectively. b – d, STM images of the substrates made by applying a different number of voltage pulses (1.4 V, 150 ms) of 5 (b), 13 (c) and 15 (d) in the BuOMT (10 mM) + iodine (0.1 mM) + NBu_4PF_6 (0.1 M) DCM solution. e, Cyclic voltammogram of polythiophene wires on iodine-covered Au working electrode in NBu_4PF_6 (0.1 M) DCM solution with a scanning rate of 1.0 V s^{-1}. Polythiophene wires were made by applying 30 pulses (1.4 V, 150 ms) in the BuOMT (10 mM) + iodine (0.1 mM) + NBu_4PF_6 (0.1 M) DCM solution. f – h, Histograms of wire-length distributions for substrates made by applying pulses (1.4 V, 150 ms) of 5, 13 and 15, respectively (Reprinted with permission from Ref. 85. Copyright Nature Materials).

step-by-step electropolymerization of 3-butoxy-4-methylthiophene (BuOMT) monomer by applying voltage pulses to the BuOMT-NBu_4PF_6 (0.1 M) DCM (as an electrolyte solution) containing iodine on Au(111), it was found that the single conjugated-polymer wires with high-density arrays and the length of 75 nm were formed on the surface of a Au(111) electrode.[85] In this study, the function of iodine is decreasing the double-layer charging, leading to the change of polymeric potential and influencing the formation of the well-organized single polythiophene wires. Herein iodine acts as a glue to attach the polythiophene wires to Au(111) surfaces.[103]

Figure 8 shows the images of the polythiophene formed by polymerization with a number of potential pulses. The STM images suggest that the epitaxial growth of polythiophene wires are propagating along the three specific directions of the Au(111) substrates. The length of the polythiophene wires shows clear dependence on the number of pulses (Figs. 8f – 8h). With the different concentrations of iodine, the results of polymerization are also different. In a low iodine concentration (0.01 mM), wires can not be created, while the higher iodine concentrations of 0.1 and 1 mM produce similar wires. Figure 9 is the schematic diagram of the mechanism for the electrochemical epitaxial polymerization in the iodine-containing system. In the mechanism, the oxidized monomer produced in the solution by the applied potential pulse reacts step-by-step with the nuclei on the iodine-Au(111) surface and propagates along the substrate lattice.

The molecular assembly and electropolymerization of 3,4-ethylenedioxythiophene (EDOT) on a bare Au(111) electrode was investigated by *in-situ* ECSTM in 0.1 M $HClO_4$.[27] It was found that both ordered and disordered domains coexisted in the EDOT adlayer, which were characterized by vacancy islands with the subsequent lifting of the reconstruction lines upon adsorption of the EDOT molecules. Electrochemical polymerization by shifting the potential positively resulted in the formation of pEDOT clusters rather than the single chain wires. This in turn resulted in the vertical polymer growth rather than propagation along the substrate lattices. Another similar result was observed by Si and coworkers in the study of electropolymerization of (4-benzeno-15-crown-5-ether)-thiophene-3-methylene-amine (BTA) molecules.[82] Figure 10 shows the typical STM images of polyBTA and its 3D modeling structures. Through controlling the substrate potential, the electropolymerization of the adsorbed BTA monomers resulted in the formation of the polymer nanoparticles or clusters distributed spontaneously over the Au(111) surface. The size of the polyBTA molecule could be controlled by the applied potential and the monomer concentration. Because of the crown ether group in these polythiophene derivatives, the prepared polyBTA films showed selective responses to potassium ions with a linear dependence of ion concentration over 4 orders of magnitude. This opens the door towards the functionalization of polythiophene nanoparticles.

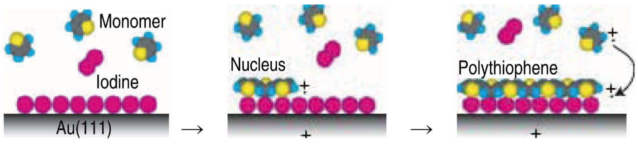


Fig. 9 Schematic diagram of the mechanism for electrochemical epitaxial polymerization in the iodine-containing system (Reprinted with permission from Ref. 85. Copyright Nature Materials).

7 Other Ways to Induce 2D Polymerization

Besides the tip-induced, light-induced and electrochemistry-induced 2D polymerization at the liquid/solid interface, many other methods were used in the polymerization, such as molecule corrals,[73] heat-induced,[113] condensation reaction[114] and others.[115-117]

Zwaneveld *et al.* used a boronate-based chemistry to form surface covalent organic frameworks (SCOFs) on Ag(111) surfaces,[118] which has been proven to be an effective method in synthesis of highly ordered three-dimensional covalent organic frameworks.[119-121] Figure 11 is the STM image of the so-called SCOFs and the chemical structure of its two monomers. The SCOFs was formed by the condensation reaction of BDBA and 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP). The size and chemical functionality of the SCOFs could be controlled by the complementary molecular building blocks, in this case of BDBA

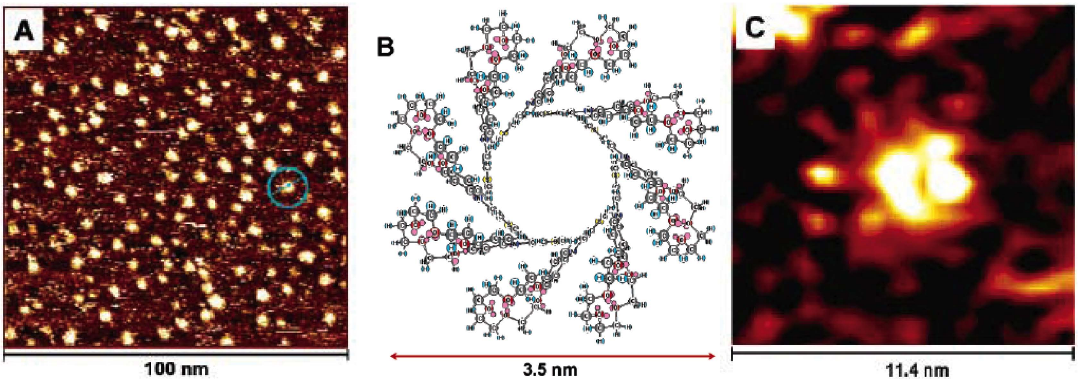


Fig. 10 Two STM images (A and C) and 3D modeling structures of (B) the eightfold oligomer with a close-up configuration. The images (A and C) acquired after cyclic voltammetric scans up to 0.95 V (*vs.* SCE) in 30 mM $HClO_4$ solution containing 2.0 mM BTA. Scan areas: (A) 100 nm × 100 nm and (C) 11.4 nm × 11.4 nm. Tunneling current (I_t) = 0.20 nA, bias voltage (V_b) = –0.05 V, and substrate potential (E_w) = 0.48 V (*vs.* SCE) (Reprinted with permission from Ref. 82. Copyright American Chemical Society).

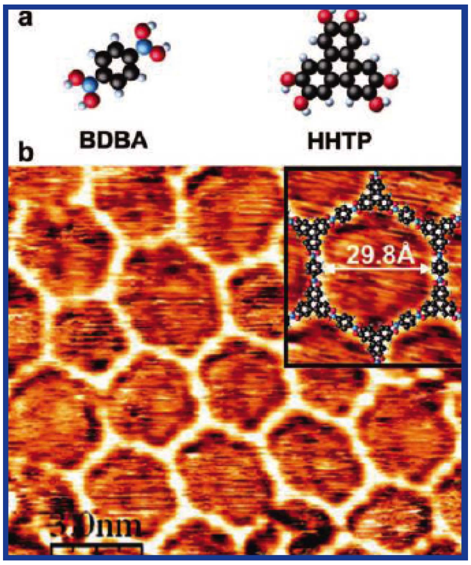


Fig. 11 SCOFs formed from BDBA and HHTP on Ag(111) surface. (a) Chemical structure of BDBA and HHTP molecules; (b) STM image of the SCOFs network showing hexagonal and other polygon structures (*e.g.*, pentagons and heptagons). The tunneling conditions were I = 1.7 nA, V = –2.2 V. The inset shows the SCOFs network with overlaid chemical structure obtained by DFT calculation (Reprinted with permission from Ref. 118. Copyright American Chemical Society).

and HHTP. In the reaction, a monolayer of HHTP was initially deposited in order to inhibit the homopolymerization of BDBA, which could also form an SCOF but with smaller pore size. Then, sequentially, BDBA and HHTP was codeposited on the Ag(111) surface; through the annealing treatment, surplus HHTP and water produced during polymerization could be ablated. From the STM image, the network was constituted by hexagonal structures with some defects present in the film. Boronate-based chemistry represents a useful way to form SCOFs, which resulted in SCOFs that extended over a very large area and showed high thermal stability. These properties are essential for further functionalization of the SCOFs and applications such as surface patterning and sensing.

Some other examples for the formation of 2D polymerization on the substrate surface have also been demonstrated under UHV conditions, for instance using thermo or substrate mediated activation of halogenated aromatic monomers.[119,122-124] However, these studies are out of the scope of this review and the readers who are interested in this area are referred to the original papers or to a recent review.[125]

8 Conclusion and Outlook

In this work, we have reviewed the recent studies on 2D polymerization at solid/liquid interface by STM, especially some methods to induce polymerization.

We mainly introduced the electrochemistry-induced, STM tip-induced and light-induced polymerization on single crystal metals and HOPG surfaces. In the electrochemistry-induced polymerization, the width and the value of the pulse potential, the concentration of the monomer, and the kinds of anion in the solution have a great influence on the polymerization. For the STM tip-induced polymerization, the height and duration of the applied potential between the tip and the sample surface are also important. Then the time and the intensity of the irradiation play an important role in the light-induced polymerization. Of course, other methods have their own advantages; heat-induced, condensation reactions are also frequently used in the polymerization on a 2D surface. However, since we limited our review to the polymerization at the solid/liquid interface, we have not gone into detail about those results which are obtained under UHV.

The polymerization products by all kinds of methods have very attractive potential applications, such as surface patterning and functionalization, molecular sensing, miniaturizing integrated circuits, molecular switch and nanoreactors. Thus, it is of great importance to study and understand the mechanism of the 2D polymerization on solid/liquid interfaces.

STM has played an important role in the characterization of assembling structures and surface reactions at the solid/liquid interface, and until now it is still the most important if not the only choice for the direct revealing of structural and electrical information at the solid/liquid interface with atomic/molecular resolution. In the foreseeable future it will still be the technique of choice for the investigation of the 2D polymer, including the fabrication, structural characterizations and applications such as nanoreactors and scaffolds of nanocircuits.

9 Acknowledgements

The work was financially supported by National Natural Science Foundation of China (20705011, 20905032, 21065005), Natural Science Foundation of Jiangxi Province (2007GZW0174, 2008GZH0028), Foundation of Jiangxi Educational Committee (GJJ09455, GJJ10389), Scientific Research Foundation for the Returned Overseas Chinese Scholars (State Education Ministry), the State Key Laboratory of Electroanalytical Chemistry (2008003), and the start-up funding of HIT and New Century Excellent Talents in University (NCET).

10 References

1. G. Binnig and H. Rohrer, *Helv. Phys. Acta*, **1982**, *55*, 726.
2. G. Binnig and H. Rohrer, *Rev. Mod. Phys*., **1987**, *59*, 615.
3. Z. Ma, Y. B. Li, K. Deng, S. B. Lei, Y. Y. Wang, P. Wang, Y. L. Yang, C. Wang, and W. Huang, *J. Phys. Chem. C*, **2010**, *114*, 11460.
4. T. Kudernac, S. B. Lei, J. A. A. W. Elemans, and S. De Feyter, *Chem. Soc. Rev*., **2009**, *38*, 402.
5. Y. B. Li, Z. Ma, K. Deng, S. B. Lei, Q. D. Zeng, X. L. Fan, S. De Feyter, W. Huang, and C. Wang, *Chem.—Eur. J*., **2009**, *15*, 5418.
6. D. Wang and L. J. Wan, *J. Phys. Chem. C*, **2007**, *111*, 16109.
7. J. A. Theobald, N. S. Oxtoby, M. A. Phillips, N. R. Champness, and P. H. Beton, *Nature*, **2003**, *424*, 1029.
8. J. V. Barth, *Annu. Rev. Phys. Chem*., **2007**, *58*, 375.
9. S. D. Feyter, A. Miura, S. Yao, Z. J. Chen, F. Würthner, P. Jonkheijm, A. P. H. J. Schenning, E. W. Meijer, and F . C. De Schryver, *Nano Lett*., **2005**, *5*, 77.
10. S. H. Wu and B. L. Zhang, *Langmuir*, **2009**, *25*, 1385.
11. S. Furukawa, K. Tahara, F. C. De Schryver, M. Van der Auweraer, Y. Tobe, and S. De Feyter, *Angew. Chem., Int. Ed*., **2007**, *46*, 2831.
12. S. Stepanow, M. Lingenfelder, A. Dmitriev, H. Spillmann, E. Delvigne, N. Lin, X. Deng, C. Cai, J. V. Barth, and

K. Kern, *Nat. Mater.*, **2004**, *3*, 229.
13. N. Lin, S. Stepanow, M. Ruben, and J. V. Barth, in "*Templates in Chemistry III*", **2009**, Vol. 287, Springer-Verlag, Berlin, 1.
14. R. V. Hameren, P. Schön, A. M. V. Buul, J. Hoogboom, S. V. Lazarenko, J. W. Gerritsen, H. Engelkamp, P. C. M. Christianen, H. A. Heus, J. C. Maan, T. Rasing, S. Speller, A. E. Rowan, J. A. A. W. Elemans, and R. J. M. Nolte, *Science,* **2006**, *314*, 1433.
15. T. Yokoyama, S. Yokoyama, T. Kamikado, Y. Okuno, and S. Mashiko, *Nature*, **2001**, *413*, 619.
16. S. B. Lei, K. Deng, Y. L. Yang, Q. D. Zeng, C. Wang, Z. Ma, P. Wang, Y. Zhou, Q. L. Fan, and W. Huang, *Macromolecules*, **2007**, *40*, 4552.
17. Z. Y. Yang, H. M. Zhang, C. J. Yan, S. S. Li, H. J. Yan, W. G. Song, and L. J. Wan, *Proc. Natl. Acad. Sci. U. S. A.*, **2007**, *104*, 3707.
18. E. Mena-Osteritz, *Adv. Mater.*, **2002**, *14*, 609.
19. M. M. S. Abdel-Mottaleb, G. Götz, P. Kilickiran, P. Bäuerle, and E. Mena-Osteritz, *Langmuir*, **2006**, *22*, 1443.
20. S. Zhang, Y. Guo, L. Wang, Q. Li, K. Zheng, X. Zhan, Y. Liu, R. Liu, and L. J. Wan, *J. Phys. Chem. C*, **2009**, *113*, 16232.
21. M. Brun, R. Demadrille, P. Rannou, A. Pron, J. P. Travers, and B. Grevin, *Adv. Mater.*, **2004**, *16*, 2087.
22. H. Glowatzki, S. Duhm, K. F. Braun, J. P. Rabe, and N. Koch, *Phys. Rev. B*, **2007**, *76*, 125425.
23. M. Kiel, K. Duncker, C. Hagendorf, and W. Widdra, *Phys. Rev. B*, **2007**, *75*, 195439.
24. L. Wang, B. J. V. Tongol, S. L. Yau, T. Otsubo, and K. Itaya, *Langmuir*, **2010**, *26*, 7148.
25. B. J. V. Tongol, L. Wang, S. L. Yau, T. Otsubo, and K. Itaya, *J. Phys. Chem. C*, **2009**, *113*, 13819.
26. B. J. V. Tongol, L. Wang, S. L. Yau, T. Otsubo, and K. Itaya, *Langmuir*, **2010**, *26*, 982.
27. L. D. S. Lapitan, Jr., B. J. V. Tongol, and S. L. Yau, *Langmuir*, **2010**, *26*, 10771.
28. Y. Song and L. Wang, *Microsc. Res. Techniq.*, **2009**, *72*, 79.
29. B. H. Huisman, J. J. P. Valeton, W. Nijssen, J. Lub, and W. ten Hoeve, *Adv. Mater.*, **2003**, *15*, 2002.
30. M. Mazzeo, D. Pisignano, L. Favaretto, G. Barbarella, R. Cingolani, and G. Gigli, *Synth. Met.*, **2003**, *139*, 671.
31. R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlund, and W. R. Salaneck, *Nature*, **1999**, *397*, 121.
32. G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, *Science*, **1995**, *270*, 1789.
33. H. J. Egelhaaf, D. Oelkrug, W. Gebauer, M. Sokolowski, E. Umbach, T. Fischer, and P. Bäuerle, *Opt. Mater.*, **1998**, *9*, 59.
34. H. Sirringhaus, N. Tessler, and R. H. Friend, *Science*, **1998**, *280*, 1741.
35. S. A. Safran, "*Statistical Thermodynamics of Surfaces, Interfaces and Membranes*", **1994**, Addison-Wesley Publishing Co., New York.
36. G. A. Sefler, Q. Du, P. B. Miranda, and Y. R. Shen, *Chem. Phys. Lett.*, **1995**, *235*, 347.
37. A. Ikai, *Surf. Sci. Rep.*, **1996**, *26*, 261.
38. W. A. Zisman, "'*The Solid/Liquid Interface—An Essential and Active Frontier of Science*' *in Interaction of Liquids at Solid Substrates*", ed. A. Alexander, **1968**, Chap. 1, Advances in Chemistry, American Chemical Society, Washington, D.C., 1 – 9.
39. B. E. Conway, "*Theory and Principles of Electrode Processes*", **1965**, Ronald Press, London.
40. R. Parsons, "*Modern Aspects of Electrochemistry*", ed. J. O'M. Bockris and B. E. Conway, **1954**, Vol. 1, Academic Press, New York, 103 – 179.
41. J. O'M. Bockris, M. A. V. Devanathan, and K. Muller, *Proc. Roy. Soc.* [London], **1963**, *274*, 55.
42. A. J. Bard and L. R. Faulkner, "*Electrochemical Methods*", **1980**, John Wiley & Sons, New York.
43. G. Jerkiewicz, "*From Electrochemistry to Molecular-Level Research on the Solid-Liquid Electrochemical Interface*", **1997**, American Chemical Society, Washington, D.C.
44. G. Binnig, H. Rohrer, C. Gerber, and E. Weibel, *Surf. Sci.*, **1983**, *131*, L379.
45. K. S. Schneider, K. T. Nicholson, D. R. Fosnacht, B. G. Orr, and M. M. Banaszak Holl, *Langmuir*, **2002**, *18*, 8116.
46. D. M. Kolb, "*Surface Reconstruction at Metal-electrolyte Interfaces*' *in Structure of Electrified Interfaces*", ed. J. Lipkowski and P. N. Ross, **1993**, VCH Publishers, 65.
47. D. Coulman, J. Wintterlin, J. V. Barth, G. Ertl, and R. J. Behm, *Surf. Sci.*, **1990**, *240*, 151.
48. R. Feidenhans, F. Grey, R. L. Johnson, and M. Nielsen, *Phys. Rev. B*, **1991**, *44*, 1875.
49. F. M. Leibsle, *Surf. Sci.*, **1995**, *337*, 51.
50. T. Orzali, D. Forrer, M. Sambi, A. Vittadini, M. Casarin, and E. Tondello, *J. Phys. Chem. C*, **2008**, *112*, 378.
51. J. Inukai, M. Wakisaka, M. Yamagishi, and K. Itaya, *Langmuir*, **2004**, *20*, 7507.
52. S.-L. Yau, Y.-G. Kim, and K. Itaya, *J. Phys. Chem. B*, **1997**, *101*, 3547.
53. P. Avouris, I. W. Lyo, and Y. Hasegawa, *J. Vac. Sci. Technol., A*, **1993**, *11*, 1725.
54. M. Böhringer, K. Morgenstern, W. D. Schneider, R. Berndt, F. Mauri, A. De Vita, and R. Car, *Phys. Rev. Lett.*, **1999**, *83*, 324.
55. S. Senapat and M. L. Berkowitz, *Phys. Rev. Lett.*, **2001**, *87*, 6101.
56. A. Dmitriev, N. Lin, J. Weckesser, J. V. Barth, and K. Kern, *J. Phys. Chem. B*, **2002**, *106*, 6907.
57. M. O. Lorenzo, C. J. Baddeley, C. Muryn, and R. Raval, *Nature*, **2000**, *404*, 376.
58. D. M. Kolb, *Prog. Surf. Sci.*, **1996**, *51*, 109.
59. J. K. Gimzewski and C. Joachim, *Science*, **1999**, *283*, 1683.
60. T. A. Jung, R. R. Schlitter, J. K. Gimzewski, H. Tang, and C. Joachim, *Science*, **1996**, *271*, 181.
61. D. M. Eigler and E. K. Schweizer, *Nature* [London], **1990**, *344*, 524.
62. T. C. Shen, *Science*, **1995**, *268*, 1590.
63. G. Dujardin, R. E. Walkup, and P. Avouris, *Science*, **1992**, *255*, 1232.
64. G. Meyer, L. Bartels, S. Zöphel, E. Henze, and K. H. Rieder, *Phys. Rev. Lett.*, **1997**, *78*, 1512.
65. L. Bartels, G. Meyer, and K. H. Rieder, *Phys. Rev. Lett.*, **1997**, *79*, 697.
66. L. Bartels, G. Meyer, K. H. Rieder, D. Velic, E. Knoesel, A. Hotzel, M. Wolf, and G. Ertl, *Phys. Rev. Lett.*, **1998**, *80*, 2004.
67. B. C. Stipe, M. A. Rezaei, W. Ho, S. Gao, M. Persson, and B. I. Lundqvist, *Phys. Rev. Lett.*, **1997**, *78*, 4410.
68. L. J. Lauhon and W. Ho, *J. Phys. Chem. A*, **2000**, *104*, 2463.
69. D. Takajo, Y. J. Okawa, T. Hasegawa, and M. Aono, *Langmuir*, **2007**, *23*, 5247.
70. G. Wegner, *Makromol. Chem.*, **1972**, *154*, 35.
71. B. Tieke, G. Lieser, and G. Wegner, *J. Polym. Sci., Polym. Chem. Ed.*, **1979**, *17*, 1631.

72. S. Nishio, D. I-i, H. Matsuda, M. Yoshidome, H. Uji-i, and H. Fukumura, *Jpn. J. Appl. Phys.*, **2005**, *44*, 5417.
73. S. P. Sullivan, A. Schnieders, S. K. Mbugua, and T. P. Beebe, *Langmuir*, **2005**, *21*, 1322.
74. G. Z. Wegner, *Naturforsch. B*, **1969**, *24*, 824.
75. Y. J. Okawa and M. Aono, *Nature*, **2001**, *409*, 683.
76. S. W. Hla, L. Bartels, G. Meyer, and K. H. Rieder, *Phys. Rev. Lett.*, **2000**, *85*, 2277.
77. S. W. Hla, G. Meyer, and K. H. Rieder, *Chem. Phys. Lett.*, **2003**, *307*, 431.
78. S. De Feyter and F. C. De Schryver, *J. Phys. Chem. B*, **2005**, *109*, 4290.
79. P. C. M. Grim, S. De Feyter, A. Gesquière, P. Vanoppen, M. Rücker, S. Valiyaveettil, G. Moessner, K. Müllen, and F. C. De Schryver, *Angew. Chem., Int. Ed.*, **1997**, *36*, 2601.
80. A. Miura, S. De Feyter, M. M. S. Abdel-Mottaleb, A. Gesquière, P. C. M. Grim, G. Moessner, M. Sieffert, M. Klapper, K. Müllen, and F. C. De Schryver, *Langmuir*, **2003**, *19*, 6474.
81. T. Takami, H. Ozaki, M. Kasuga, T. Tsuchiya, Y. Mazaki, D. Fukushi, A. Ogawa, M. Uda, and M. Aono, *Angew. Chem., Int. Ed.*, **1997**, *36*, 2755.
82. P. C. Si, Q. J. Chi, Z. S. Li, J. Ulstrup, P. Juul Møller, and J. Mortensen, *J. Am. Chem. Soc.*, **2007**, *129*, 3888.
83. L. Y. Ou Yang, C. Z. Chang, S. H. Liu, C. G. Wu, and S. L. Yau, *J. Am. Chem. Soc.*, **2007**, *129*, 8076.
84. G. Z. Xu, D. P. Woodruff, N. Bennett, M. Elliott, and J. E. Macdonald, *Langmuir*, **2010**, *26(11)*, 8174.
85. H. Sakaguchi, H. Matsumura, and H. Gong, *Nat. Mater.*, **2004**, *3*, 551.
86. Y. H. Lee, C. Z. Chang, S. L. Yau, L. J. Fan, Y. W. Yang, L. Y. Ou Yang, and K. Itaya, *J. Am. Chem. Soc.*, **2009**, *131*, 6468.
87. B. J. Grevin and P. Rannou, *Nat. Mater.*, **2004**, *3*, 503.
88. R. Wen, G. B. Pan, and L. J. Wan *J. Am. Chem. Soc.*, **2008**, *130*, 12123.
89. X. R. Miao, C. M. Chen, J. Zhou, and W. L. Deng, *Appl. Surf. Sci.*, **2010**, *256*, 4647.
90. Y. Lee, S. Chen, H. Tu, S. Yau, L. Fan, Y. Yang, and W. Dow, *Langmuir*, **2010**, *26*, 5576.
91. S. L. Yau, Y. H. Lee, and C. Z. Chang, *J. Phys. Chem. C*, **2009**, *113*, 13758.
92. S. Chen, H. L. Tu, C. G. Wu, and S. L. Yau, *J. Phys. Chem. C*, **2010**, *114*, 8493.
93. W. S. Huang, B. D. Humphrey, and A. G. MacDiarmid, *J. Chem. Soc., Faraday Trans. 1*, **1986**, *82*, 2385.
94. D. Orata and D. A. Buttry, *J. Am. Chem. Soc.*, **1987**, *109*, 3574.
95. T. Takei, Y. Kobayashi, H. Hata, Y. Yonesaki, N. Kumada, N. Kinomura, and T. E. Mallouk, *J. Am. Chem. Soc.*, **2006**, *128*, 16634.
96. J. Huang, S. Virji, B. H. Weiller, and R. B. Kaner, *J. Am. Chem. Soc.*, **2003**, *125*, 314.
97. Y. Ma, S. R. Ali, L. Wang, P. L. Chiu, R. Mendelsohn, and H. He, *J. Am. Chem. Soc.*, **2006**, *128*, 12064.
98. H. Liu, J. Kameoka, D. A. Czaplewski, and H. G. Craighead, *Nano Lett.*, **2004**, *4*, 671.
99. L. H. Mascaro, D. Goncalaves, and L. O. S. Bulhões, *Thin Solid Films*, **2004**, *461*, 243.
100. S. J. Choi and S. M. Park, *J. Electrochem. Soc.*, **2002**, *149*, E26.
101. H. Tang, A. Kitani, and M. Shiotani, *Electrochim. Acta*, **1996**, *41*, 1561.
102. L. J. Duić, Z. Mandić, and F. Kovačiček, *J. Polym. Sci., Part A: Polym. Chem.*, **1994**, *32*, 105.
103. P. Samorí, N. Severin, K. Müllen, and J. P. Rabe, *Adv. Mater.*, **2000**, *12*, 579.
104. L. J. Wan, *Acc. Chem. Res.*, **2006**, *39*, 334.
105. S. D. Feyter, A. Gesquière, M. M. Abdel-Mottaleb, P. C. M. Grim, and F. C. De Schryver, *Acc. Chem. Res.*, **2000**, *33*, 520.
106. N. Haddour, S. Cosnier, and C. Gondran, *J. Am. Chem. Soc.*, **2005**, *127*, 5752.
107. L. C. Giancarlo and G. W. Flynn, *Acc. Chem. Res.*, **2000**, *33*, 491.
108. X. Qiu, C. Wang, Q. Zeng, B. Xu, S. Yin, H. Wang, S. Xu, and C. Bai, *J. Am. Chem. Soc.*, **2000**, *122*, 5550.
109. S. B. Lei, C. Wang, S. X. Yin, H. N. Wang, F. Xi, H. W. Liu, B. Xu, L. J. Wan, and C. L. Bai, *J. Phys. Chem. B*, **2001**, *105*, 10838.
110. S. Clair, S. Pons, A. P. Seitsonen, H. Brune, K. Kern, and J. V. Barth, *J. Phys. Chem. B*, **2004**, *108*, 14585.
111. J. V. Barth, J. Weckesser, G. Trimarchi, M. Vladimirova, A. D. Vita, C. Z. Cai, H. Brune, P. Günter, and K. Kern, *J. Am. Chem. Soc.*, **2002**, *124*, 7991
112. W. Obretenov, U. Schmidt, W. J. Lorenz, G. Staikov, E. Budevski, D. Carnal, U. Müller, H. Siegenthaler, and E. Schmidt, *J. Electrochem. Soc.*, **1993**, *140*, 692.
113. S. Boz, M. Stöhr, U. Soydaner, and M. Mayor, *Angew. Chem., Int. Ed.*, **2009**, *48*, 3179.
114. S. Weigelt, C. Busse, C. Bombis, M. M. Knudsen, K. V. Gothelf, T. Strunskus, C. Wöll, M. Dahlbom, B. Hammer, E. Laegsgaard, F. Besenbacher, and T. R. Linderoth, *Angew. Chem., Int. Ed.*, **2007**, *46*, 9227.
115. A. Gourdon, *Angew. Chem., Int. Ed.*, **2008**, *47*, 6950.
116. X. N. Zhang, D. G. de Oteyza, Y. Wakayama, and H. Dosch, *Surf. Sci.*, **2009**, *603*, 3179.
117. L. Santos, J. Ghilane, P. Martin, P. C. Lacaze, H. Randriamahazaka, and J. C. Lacroix, *J. Am. Chem. Soc.*, **2010**, *132*, 1690.
118. N. A. A. Zwaneveld, R. Pawlak, M. Abel, D. Catalin, D. Gigmes, D. Bertin, and L. Porte, *J. Am. Chem. Soc.*, **2008**, *130*, 6678.
119. A. P. Cote, H. M. El-Kaderi, H. Furukawa, J. R. Hunt, and O. M. Yaghi, *J. Am. Chem. Soc.*, **2007**, *129*, 12914.
120. H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortes, A. P. Côté, R. E. Taylor, M. O'Keeffe, and O. M. Yaghi, *Science*, **2007**, *316*, 268.
121. R. W. Tilford, W. R. Gemmill, H. C. zur Loye, and J. J. Lavigne, *Chem. Mater.*, **2006**, *18*, 5296.
122. L. Grill, M. Dyer, L. Lafferentz, M. Persson, M. V. Peters, and S. Hecht, *Nat. Nanotechnol.*, **2007**, *2*, 687.
123. R. Gutzler, H. Walch, G. Eder, S. Kloft, W. M. Heckl, and M. Lackinger, *Chem. Commun.*, **2009**, 4456.
124. M. Bieri, M. Treier, J. Cai, K. Aït-Mansour, P. Ruffieux, O. Gröning, P. Gröning, M. Kastler, R. Rieger, X. Feng, K. Müllen, and R. Fasel, *Chem. Commun.*, **2009**, 6919.
125. J. A. A. W. Elemans, S. Lei, and S. De Feyter, *Angew. Chem., Int. Ed.*, **2009**, *48*, 7298.