Interfacial molecular assembly and surface patterning

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Abstract **Based on a brief review of the traditional surface patterning research, this article introduces the recent progress in the research on surface patterning via molecular self-assembly. Because the size scale of molecular self-as- semblies is in the range of 1—100 nm, the method of molecular self-assembly can easily lead to the construction of ordered structures in nanometer scale, and thus break through the size limit of traditional lithography. Some novel ways of molecular self-assembly for surface patterning are particularly introduced in this review, including supramo- lecular architecture at interface, chemisorption of dendron thoils, and surface aggregation of bolaform amphiphiles. Provided that we know more and more about the basic principles governing the surface morphology, it is believed that interfacial molecular assembly would be a very competitive supramolecular technique, and a potential application in many fields such as surface property adjustment, organic patterned devices, surface molecular recognition, and combinatorial chemistry is greatly anticipated.**

Keywords: molecular self-assembly, patterned surface, nanostructures.

Surface patterning is to fabricate well-defined surface structures ordered at least in one lateral direction. It has fundamental as well as applied significance in many fields like supramolecular science, materials science, microelectronics, and even cell biology[1]. Surface patterning is mainly used to monitor surface properties. Surface structure in micro-scale can be applied to controlling surface adhesion, friction, and wetting properties of the materials, which are closely related to intermolecular interaction and surface topology. Selective adhesion and surface specific recognition require an accurate control of surface anisotropic property. In the field of microelectronics, an attempt is already made to use patterned materials for high density magnetic storage media. The emergence of quantum dot laser, quantum cascade laser, and single electron diode has changed the basic concept of traditional devices. In the field of cell biology, patterned surface can be used to adjust the spatial distribution of cells, to develop rapid diagnosis, and to construct neural network[2]. A potential application of the patterned surface in the fields of nano-reactors, micropatterned devices, combinatorial chemistry and drug screening is also greatly anticipated.

Surface patterning can be accomplished by many techniques. Among them, lithography is undoubtedly a traditional and widely used method. No matter what kind of an electromagnetic exposure such as X-ray and UV light is used, the operational principle is almost the same. Firstly, the electromagnetic exposure is used to induce a chemical transformation of the molecular structure of the material and forms a latent image; secondly, the latent image becomes an embossing structure by etching. There exists a resolution limit for lithography due to the diffraction effect. As the exposure wavelength becomes shorter, the resolution can be enhanced. For example, electron beam based etching can realize surface structure in the size scale of nanometers; however, it is very hard to operate in large areas.

The scanning probe based micromaching method has been used to make any type of patterned images. The patterned structures are mainly formed by either the tip-induced local transformation or local deposition. A type of microcontact printing has been developed systemically by Whitesides et al.[3,4]. Its basic principle is the combination of photolithography and the self-assembled monolayer. For example, a designed patterned image at silicon wafer is prepared by etching first, and then the patterned image is transferred with polydimethylsiloxane (PDMS) to obtain an elastomeric stamp. The rubber stamp “inked” with appropriate molecules, such as hexadecanethiol, is then placed in contact with the gold surface, producing a patterned layer onto the gold surface that is exactly the negative image of the master stamp. The principal advantage of this technique lies in its easiness of fabrication and adjustment of patterned shape. However, the preparation of a rubber stamp is still based on usual photolithography, and therefore, with this technique we cannot overcome the resolution limit.

Interfacing molecular assembly, as an important direction of supramolecular science, has gained rapid progress recently. In contrast with the molecular self-assem- bly in solution, because of the influence of two-dimen- sional space of substrate, molecular assembly at interface is in a confined state in the view of time and space. Thus we can deduce reasonably that interfacial molecular assembly is a new method capable of forming ordered surface structure. It is well known that some organic molecules and polymers can form diversified supramolecular structures in solution, e.g. laminar, spherical, disc-like and cylindrical shapes. But till now, it is still a big challenge for chemists to understand how the molecules spreading at either gas/liquid or liquid/solid interface organize spontaneously and collectively to form unique two- or three-dimensional patterned structures. Because the size range of molecular assemblies is about 1—100 nm and no photolithography is used, we can figure out that the patterned structure formed by interfacing molecular assembly can easily overcome the resolution limit of the conventional photolithography. In this review, we will introduce briefly three methods of interfacial molecular assembly, i.e. supramolecular architecture at interface, chemisorption of dendron-thoils, and surface aggregation of bolaform amphiphiles, to demonstrate primarily our successful attempts in using the interface molecular assembly for fabrication of patterned surface. Although the microphase separation of block copolymers can lead to the formation of rich and advanced organized structures, we cannot have space herein to discuss it, since there are so many original and review articles already published for references[5,6].

1 Supramolecular architecture at interface

It is well known that some amphiphiles spreading at air/water interface can form monolayer and by the Langmuir-Blodgett (LB) method it can be transferred vertically onto solid substrate to form the LB monolayer and multilayer. The formation of such a monolayer is based on the induced organization by external surface pressure, and thus the resulting monolayer is in a meta-stable state. There will appear many defects later on in the LB multilayer, because of the relaxation or post re-crystallization. Though it seems very hard to obtain the defect-free film, if conversely thinking, is it possible to make full use of the defect, and to organize it to form ordered surface structures in nanometer scale?

Upon transferring the monolayer of L-α-dipalmitoyl phosphatidycholine (DPPC) onto a mica sheet, Gleiche et al.[7] found that DPPC can form patterned surface structure, as shown in fig. 1. Different from that of traditional method for LB film, the constant surface pressure for transferring is fixed at very low value, only ca. 3.0 mN/m; and the vertical transferring speed is rapidly up to 1000 μm/s. Scanning force microscope (SFM) has shown that

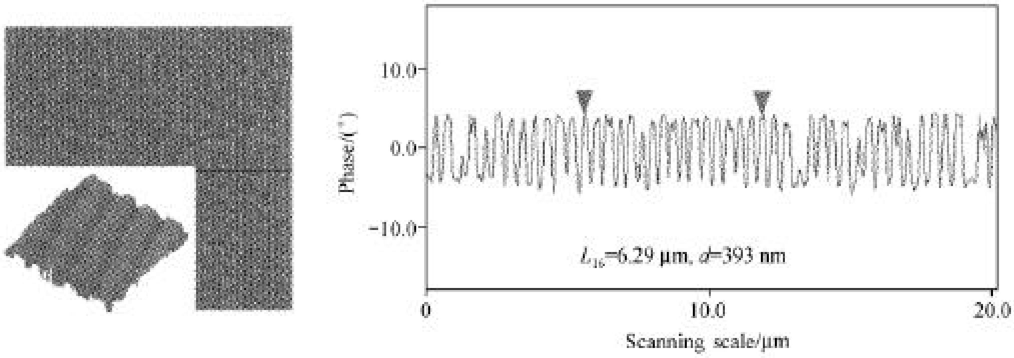

Fig. 1. The monolayer of DPPC rapidly transferred onto a mica sheet (left). SFM (right) has shown that this patterned structure is of anisotropic wetting properties in controlled way. L_{16} is the width of 16 stripes, and d is periodical spacing.

this patterned structure is of anisotropic wetting properties in controlled way; for example, a hydrophilic groove of 200 nm in width, and a hydrophobic stripe of 800 nm in width. The depth of the groove is exactly the same as the length of DPPC amphiphile. This technique can make such a nice surface structure not only fast and in large areas but also with good reproducibility. They have also found that the size of the groove and stripe can be fine-tuned by changing the temperature of subphase and transferring speed. In addition, the dust and impurity have a great influence on the formation of patterned structure. This patterned structure can be used as a matrix of high selectivity. By use of the anisotropic wetting properties of grooves and stripes, one can expect to deposit typical materials along the groove, e.g. Au_{55}, $FeCl_3$, and dyes, based on the anisotropic wetting and dewetting progress, capillary force and electrostatic interaction. One can infer that this type of patterned structure is able to form surface material with unique architecture. Its application in chemical and biochemical nano-reactors, and in analytical separation technique of high efficiency could also be anticipated.

2 Surface aggregation of amphiphiles

Amphiphiles can self-organize in solution to form supramolecular structures of sphere, cylinder and lamella. These different forms of aggregation are dependent on not only the chemical structure of the amphiphiles, but also environmental conditions like concentration, ionic stren- gth and pH value. Herein, what we concern the most is how the solid substrate influences the aggregation structures of amphiphile in solution. In other words, it is possible to accomplish ordered surface structure based on the surface aggregation of amphiphiles.

Manne et al.[8] were the first to use SFM in observing directly the aggregation behavior of amphiphile tetradecyl trimethylammonium bromide (C_{14}TAB) at solid substrates. It was found that the morphology of the aggregates is closely related to the solid substrates. When the concentration of the amphiphile is 7 mmol/L, twice its critical micelle concentration (CMC), this cationic surfactant can form a structure of crooked stripe with (5.3±0.2) nm in width on mica sheet. In the same condition, it forms irregular domain structure on the surface of amorphous silicon oxide.

Recently, Gao et al. [9] published their results of the interfacing aggregation of bolaform amphiphile bearing azobenzene. When the concentration is above its CMC, the bolaform amphiphile forms ordered stripes on mica sheet that are separated from each other by about 10 nm, as shown in fig. 2. The nano-size stripes can be influenced by many factors, such as concentration, ionic strength, length of spacer and so on. The structure of ordered stripes can be formed by bolaform amphiphile with long spacer, while similar ordered structure cannot be formed as for that bolaform amphiphile with short spacer. As sodium perchlorate is added, the structure of ordered stripes can become crooked gradually, and finally completely disappear. This could be related to the fact that the addition of electrolyte changes the interaction between bolaform amphiphile and mica substrate. Till now, we are still not able to explain why it forms such a long-range ordered structure.

But we believe it should be related to the substrate inducement effect. When a kind of modified mica sheet with rhombus holes is used as substrate, we found that the bolaform amphiphile only aggregates around the holes, and an interesting finding is that the orientation of the nano-stripes is in parallel with one edge of the rhombus hole.

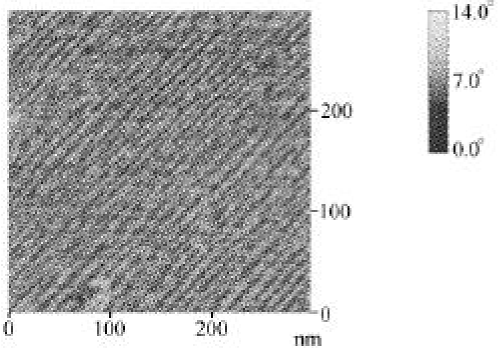

Fig. 2. The interfacing aggregation of bolaform amphiphile bearing azobenzene has shown nano-stripe structure as reviewed by SFM.

3 The chemisorption of dendrimer

Dendrimers are a type of hyperbranched molecules, the parameters of their size, shape, topology structure, surface chemistry, inner void, molecular flexibility, etc. can be precisely controlled at molecular level. The main theme that we concerned is how to combine the dendrimer chemistry with self-assembled film and to realize the control of surface morphology through the interfacial assembly of dendrimer.

For this purpose, Zhang et al.[10,11] have designed and synthesized a series of polyether dendrons with focal point of thiol group, as shown in fig. 3. Gold-covered glass slides were dipped into THF solution of a polyether dendron thiol and kept for 24 h. Then the dendron-coated gold slides were rinsed with THF and dried. Surface-enhanced Raman scattering spectroscopy has confirmed that dendron thiols are chemisorbed on the gold surface. Scanning tunneling microscopy (STM) was used to study the self-assembled monolayer of a dendron thiol on gold surface, and the ordered regions were observed locally. When annealing the sample at 70℃ for about 4 h, we could see the increased size of the ordered region, with high regularity and in long-range order. In addition, with an increase of the bias voltage of STM, we could observe that some defects are induced, which provides a further proof that ordered stripes are formed by the dendron thiol and are not caused by artifacts of the gold substrate itself. The patterned stripes are closely related to the size of the dendrons; for example, the widths of the stripes are 2.4, 3.1 and 4 nm for the first generation, second generation, and third generation of polyether dendron, respectively. Therefore, the surface structure within the scale of several nanometers can be obtained easily by controlling the size of dendrimer. The reason responsible for long-range order is still unclear. But we speculate that it should be related to a synergetic effect of interfacial chemisorption, substrate inducement and intermolecular ð-ð stacking.

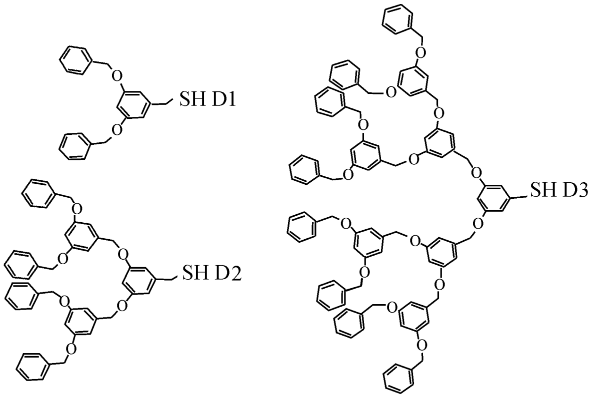

Fig. 3. Polyether dendrimer with focal point of thiol group. D1, D2 and D3 are the molecules of generation 1 to generation 3.

Recently, we designed and synthesized another series of novel dendron thiols bearing hydrophilic, hydrophobic, and hydrophilic/hydrophobic groups at their peripheries. Due to the existence of confined-nanophase separation, we have found that the dendron thiol bearing both hydrophilic and hydrophobic groups at the periphery can form ordered honeycomb structure on gold surface. Considering the rich structural variation of dendrimers, we can predict that dendrimer chemistry may provide a type of promising nanopatterning materials.

4 Concluding remarks

Interfacial molecular assembly and surface patterning are a new direction of supramolecular science and technology. There are many scientific problems to be resolved. On one hand, because of the close correlation of interfacial molecular aggregation and molecular structure, the development of this field lies in designing and synthesizing a series of new material able to self-assemble. On the other hand, because self-assembly at interface can be influenced strongly by environmental condition, we need to pay much attention to the manipulative rule of morphology through changing environmental condition. Another target is to combine the theoretical calculation and computer simulation in understanding the basic principles behind and thus guiding the design and synthesis of materials. In view of application, one should attach importance to strengthening the interaction between ordered structure and substrate to obtain stable patterning surface, e.g. through molecular design or substrate modification. Considering from aspect of function, we should attach importance to introducing specific groups, so as to realize specific functional domains, and even to realize reversible pattern change. In short, to construct ordered patterning surface via interfacial molecular assembly is just underway, and there is no doubt that this is a new field that chemists can make full use of their imagination.

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