



Manipulation of thin film assemblies: Recent progress and novel concepts

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ABSTRACT

Manipulation of self-assembly processes to construct predesigned supramolecular architectures in a controllable manner is of utmost importance in the field of nanotechnology for the development of application-oriented devices. We here summarize recent progress in the current strategies for the manipulation of thin film assemblies on solid surfaces and at interfaces, as well as in freestanding thin film structures. We also highlight our recent progress including a description of the concept of hand-operating nanotechnology for controlling thin film assemblies at dynamic interfaces. This review is organized into three sections: (i) functionalization and manipulation of solid surfaces to assist molecular self-assembly; (ii) manipulation of freestanding ultrathin films by self-assembly; and (iii) molecular assembly at dynamic interfaces.

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1. Introduction

Recent years have witnessed an enormous growth in the field of thin film materials fabricated using bottom-up approaches, which rely mainly on the concept of self-assembly of molecular building blocks. To date, several researchers have made significant contributions to the development of self-assembling processes by applying an interdisciplinary research philosophy [1^{**}]. Despite the great success of supramolecular techniques for the construction of hierarchical structures at the nanoscale [2,3], only a few practical devices have been implemented. This is mostly because of difficulties entailed in obtaining structures suitable for specific applications, since spontaneous molecular self-assembly, which is due to weak intermolecular interactions, only yields specific aggregated nanostructures with little possibility of controlling the structures obtained. Needless to say, achieving manipulation of thin film assemblies on demand would be an important step for the development of nanotechnology. One promising method lies in surface- and interface-related technologies, which offer great potential for the reliable manufacture of molecular self-assemblies at the nanoscale [4,5]. This is because

molecules confined at two-dimensional surfaces and interfaces tend to assemble under different constraints, with respect to their conformations/orientations and interactions, from those prevailing in three dimensional systems where self-assembly has many more degrees of freedom available.

Basically, thin film assemblies can exist at solid surfaces, at fluid–fluid interfaces or in the absence of a substrate or interface. On solid surfaces, supramolecular thin film assemblies can be manipulated through surface functionalization and surface patterning, and have good potential for integration into artificial devices. At fluid–fluid interfaces, another distinct aspect of thin film assemblies exists in their advanced dynamism, which is anticipated to lead to preparation of various stimuli-responsive systems such as molecular recognition receptors or molecular machines. Thin film assemblies lacking substrate or interfacial support (i.e. freestanding thin films) are flexible and lightweight, and might lead to application such as perm-selective and sensing membranes [6^{*}]. All of these thin film materials could be used in the construction of soft and smart devices that can operate dynamically in response to a variety of external stimuli or chemical/physical treatments, so that studies on two-dimensional molecular assemblies are meaningful for the adaptation of thin film materials.

In this review, we would like to focus on recent progress in the current strategies used for manipulation of thin film assemblies on solid surfaces or at interfaces as well as of freestanding structures. We have organized this review into three sections: (i) manipulation of solid surfaces to aid molecular self-assembly, wherein the surface functionalization and surface patterning methods are discussed with respect to regulate the

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two-dimensional molecular organization on static solid supports; (ii) manipulation of freestanding ultrathin films using self-assembly, where the current methods are presented together with detailed discussion on well-ordered nanofilms; (iii) molecular assembly at dynamic interfaces, wherein recent advances in the functional capabilities of molecular ensembles at an air–water interface for molecular recognition and operation of molecular machines are presented, and finally we highlight the developments in characterization techniques for studying self-assembly processes at dynamic liquid interfaces, leading to our original concept, hand-operating nanotechnology, as a ubiquitous method for controlling thin film assemblies at dynamic interfaces. At the end of each section, we will briefly summarize our opinions and future perspectives. We anticipate that this review will prove instructive not only regarding current technologies, but also to apply them in the construction of artificially prepared thin film materials for use in the near future.

2. Manipulation of solid surfaces to aid molecular self-assembly

Molecular self-assemblies on surfaces exhibit different characteristics to those in the bulk state, such as in solution or thick films, due to concerted interactions driven by entropy effects, van der Waals interactions, electrostatics and hydrogen bonding. However, by tailoring the surface morphology of solid substrates, thereby promoting desirable interactions between the solid substrate and the assembling materials, we can obtain controllable and well-ordered thin film assemblies. This method is known as surface-induced assembly wherein the surface of the solid substrate directs the molecular self-assembly process. In this section, we will review the currently employed surface modification strategies using chemical functionalization and surface patterning to aid molecular self-assembly into the desired supramolecular structures.

2.1. Surface functionalization

There has been a wide range of surface functionalization strategies applied to solid substrates to direct molecular self-assembly. These include tuning the hydrophobicity or hydrophilicity of the surface by growing self-assembled monolayers (SAMs), treating the substrate with reactive gases, tailoring the wettability of the surface of the substrates externally, introducing electrical charges on the substrate and many other methods [7]. Although the general concept of surface functionalization of solid substrates for self-assembly has been already investigated and widely applied, recent progress in this field and related newly developed methods will be reviewed here.

Metal surfaces modified with thiol molecules have been utilized for guiding the self-assembly of a variety of materials. In a recent report by Rhee and coworkers [8], alkanethiol SAM on Au(111) surface was used to selectively adsorb massive multi-walled carbon nanotubes (MWCNTs). They present a novel method involving selective replacement reaction, wherein the MWCNTs modified with dithiolate are anchored onto alkanethiol SAMs on gold surface by a specific exchange reaction, depending on the alkyl chain lengths of the dithiolates attached to MWCNTs and the thiolate forming SAMs.

Surface modification is also employed for the controlled assembly and immobilization of biopolymeric materials. Theato and coworkers have recently presented a strategy to produce stable and adherent thin reactive coatings on various substrates suitable for specific protein immobilization [9]. They used an inorganic–organic hybrid graft copolymer, poly(methylsilsesquioxane)-poly(pentafluorophenyl acrylates), to form the reactive coating onto gold, polycarbonate, polytetrafluoroethylene and glass substrates. By dipping these functionalized substrates in a solution of the desired amine, specific binding sites for protein assembly such as biotin, L-thyroxine and folic acid, were anchored on the surface. Furthermore, they also studied the controlled assembly of proteins such as streptavidin, pre-albumin and folate-

binding protein using several spectroscopic and microscopic techniques. The main advantages of this strategy are its simplicity and substrate-independent nature of the reactive coating to control the assembly of proteins.

In a recent investigation by Blasie and coworkers, surface functionalization of solid substrates was employed to covalently attach ensembles of 4-helix bundle peptides formed as Langmuir monolayers at the air–water interface (Fig. 1) [10]. In this study, they first alkylated the surface of Si wafer and fused silica substrates with 3-aminopropyltrimethylethoxysilane layer and subsequently attached the linker, succinimidyl 4-(*N*-maleimidomethyl)cyclohexane-1-carboxylate, which is capable of forming a covalent bond with the sulfur atom in the terminal cysteine residue of the peptide. The Langmuir monolayer of the peptide formed at the air–water interface was assembled onto these functionalized substrates by horizontal lifting (Langmuir–Schaefer) deposition. The key advantage of this approach is the resulting covalent linkage between the substrate and the assembled biomolecules, which is expected to increase the stability of thin film structures on solid surfaces in comparison to physisorption. Another unique aspect is the control possibility of the distance between the substrate and the peptide by changing the linker length.

Dip-pen nanolithography has gained a lot of attention ever since its first demonstration by Mirkin and coworkers [11]. This nanofabrication technique based on scanning probe microscopy (SPM) uniquely combines direct-write soft matter compatibility with high resolution and registry of atomic force microscopy (AFM), thus making it a powerful tool for depositing soft and hard materials in the form of stable and functional architectures on a variety of substrates. Several applications including controllable molecular assembly have been recently concisely reviewed [12]. Recently, Frechet and coworkers made a substantial step forward in utilizing the dip-pen nanolithography technique to functionalize surfaces with benzoquinone and propyltrichlorosilane mixed monolayers and demonstrated multiplexed directed assembly of complementary materials [13]. They functionalized the surface of the substrate with more than one type of functionality in a spatially resolved fashion, wherein specific oxidative and reductive regions having affinity to different molecules were generated. A scanning probe was used to create two orthogonal types of functionality within a dense, electrochemically-active mixed monolayer via a simple modulation of the applied surface bias. The main advantage of this method is that each of the two surface functionalities was used independently to locally assemble complementary materials such as donor and acceptor molecules via self-assembly. For example, they achieved localized assembly of pentathiophene dimethylchlorosilane and a fullerene derivative on oxidized and reduced regions prepared by the dip-pen nanolithography, respectively. This directed-assembly of both *p*- and *n*-type semiconducting molecules on the same plane highlights the possibility of surface assembly of complementary heterogeneous structures in the fabrication of more complex nanoarchitectures.

Molecular recognition directed self-assembly is another novel concept employed in the surface functionalization strategy, in order to fabricate controlled molecular assemblies with desirable morphologies. Valiokas and coworkers developed a technique combining dip-pen nanolithography and molecular recognition to form reversible assembly of functional protein complexes in nanoscopic surface domains [14]. The AFM tip inked with oligo(ethylene glycol) disulfide bearing terminal biotin groups was used for the functionalization of gold surface achieving line widths below 100 nm. The highly specific recognition capability of biotin for streptavidin has been employed for the fabrication of functional nanostructures. Subsequently, this biotin–streptavidin functionalization on the gold substrate was utilized for the formation of a multivalent chelator domain for reversible assembly of histidine tagged proteins via the attachment of a biotin derivative bearing tris-nitriloacetic acid. This method offers a facile route for the construction and analysis of functional protein-based nanoarchitectures.

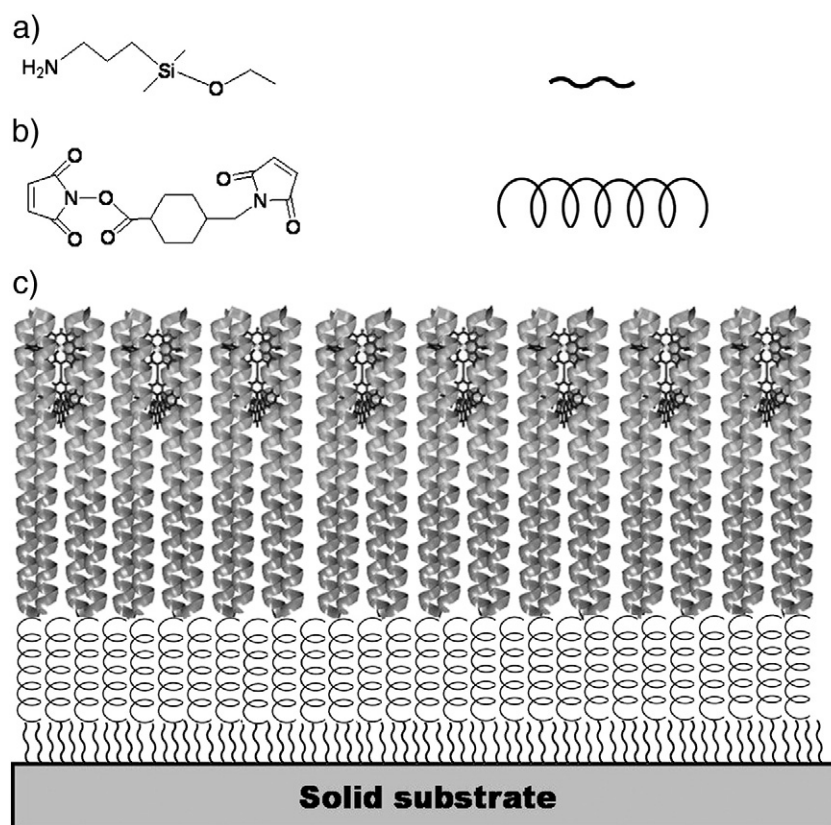


Fig. 1. Chemical structures of (a) 3-aminopropyltrimethoxysilane and (b) succinimidyl 4-(N-maleimidomethyl) cyclohexane-1-carboxylate. (c) Schematic illustration of surface functionalization for the peptide assembly on solid substrates.

2.2. Surface patterning

Surface patterning is one of the widely used strategies to control the self-assembly of molecules into desired hierarchical supramolecular

architectures. The surface patterning method can be broadly classified into two approaches: (i) top-down approach such as lithography or (ii) bottom-up approach such as layer-by-layer (LbL) assembly and Langmuir–Blodgett (LB) technique. In addition, surface patterning is

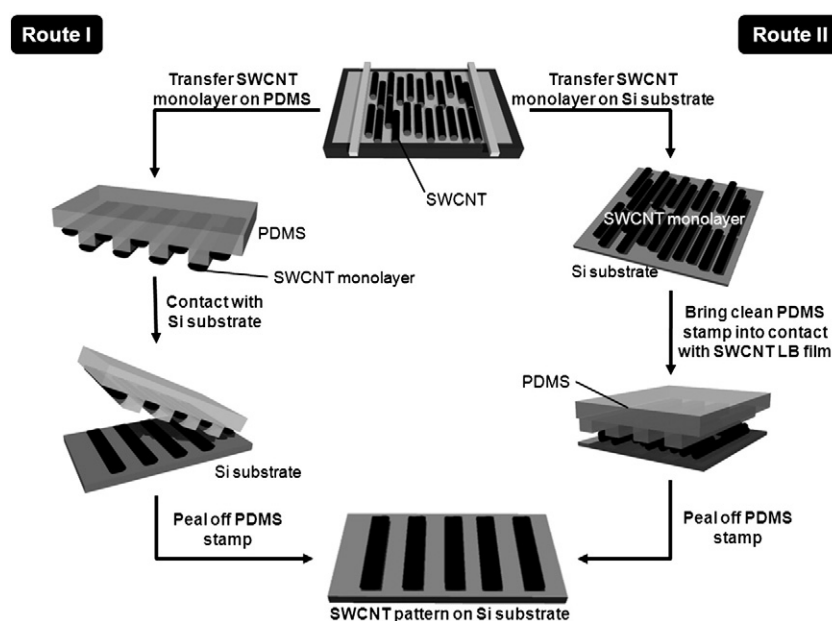


Fig. 2. Schematic representation of the fabrication procedure of patterned SWNTs by using a combination of LB method and soft lithography; route I: microcontact printing (μCP) method; route II: lift-up method.

performed either on bare or functionalized substrates. A brief outline of the currently available methods has been summarized by Cremer [15], although it did not directly establish the importance of surface patterning for manipulation of self-assembly processes. Hence, in this review, we would like to specifically focus on some representative surface patterning strategies that have been developed recently for manipulating self-assembled thin films on solid substrates.

Kim and coworkers used a surface patterning technique based on microcontact printing (μ CP) and LB deposition to assemble single-walled carbon nanotubes (SWCNTs) into hierarchically aligned structures having both high density and ordered orientation [16*]. A pre-patterned polydimethylsiloxane (PDMS) stamp was used as a template to create aligned hierarchical pattern of SWCNT on functionalized Si substrates via two different routes, one involving microcontact printing and another by lift-up process, as shown in Fig. 2. In the microcontact printing route, a Langmuir film of SWCNT formed at an air–water interface was transferred onto the PDMS stamp and subsequently, the stamp was kept in contact with the Si substrate in order to imprint SWCNTs onto it. Finally, the stamp was peeled off leaving the patterned SWCNT assembly on the Si substrate. On the other hand, in the lift-up process, the Langmuir film of SWCNT at the air–water interface was first transferred onto a Si substrate, then a clean PDMS stamp was brought into contact with the LB film and subsequently peeled off leaving the patterned SWCNTs on the Si substrate. They indicated that the patterns formed by lift-up process (route II) produced better feature shapes up to the micrometer scale compared to those obtained by using the microcontact printing method (route I). Both of these patterning techniques combine the unique advantages of both soft lithography and the LB method for manipulating hierarchical self-assembly.

Patterning of graphene to fabricate periodic nanostructures with controllable periodicities is one of the important milestones achieved in graphene science and may have several implications for the electronics industry. This was achieved by Tour and coworkers, who developed a technique based on the self-assembly of monodisperse colloidal microspheres to form two-dimensional arrays of patches with varying periodicity and distances between the graphene neck widths [17]. This material exhibited promising electronic properties featuring an ambipolar electric field effect typical for graphene with mobilities of 870 and 460 $\text{cm}^2/\text{V}^{-1}\text{s}^{-1}$ for holes and electrons, respectively.

Colloidal lithography is one of the upcoming self-assembly based techniques for the fabrication of well-ordered nanostructures. The spherical shape and ordered packing of colloidal crystals favor the successful fabrication of two-dimensional nanostructured arrays. These materials have been employed as masks or templates for several physical processes such as evaporation, deposition, etching, imprinting and so on, in order to fabricate the desired supramolecular assemblies. In addition, this technique is facile, inexpensive and reproducible for the fabrication of a variety of nanostructured thin film assemblies in a controllable manner. In a recent article, Zhang and coworkers reported a simple method to fabricate two-dimensional periodic non-close-packed (ncp) arrays of colloidal microspheres with controllable lattice spacing, lattice structure, and pattern arrangements [18]. They employed the soft lithography technique with controlled deformation of PDMS elastomer to convert 2D hexagonal close-packed (hcp) silica microspheres into ncp arrays. These structures are expected to serve as prototypes of optical materials.

In the field of biomolecular materials, both surface patterning for the assembly of biomolecules (proteins, lipids etc.) and also surface patterning using biomolecules (DNA, peptides etc.), have gained considerable interest in recent years. The article by Ekbal and Liedberg highlights the importance of surface patterning in biology especially for protein adsorption studies [19]. The authors present a detailed overview of both direct and indirect patterning methods such as elastomeric stamps, microfluidics, ink-jet printing, photolithography, and they also discuss the specifics of protein adsorption on the resulting materials. On the other hand, biomolecules, especially DNA, have been used for the rational design and construction of nanoscale

patterns. In this regard, scaffolded DNA origami has emerged as one of the most promising assembly techniques in DNA nanotechnology with a broad range of applications including the controlled organization of a plethora of nanomaterials including metal nanoparticles, proteins and carbon nanotubes. As an example, Yan and coworkers utilized the DNA origami concept for self-assembly of metal nanoparticles into discrete architectures [20]. In addition to assembling monomeric, dimeric and trimeric silver nanoparticles–DNA origami conjugates, gold–silver nanoparticle hybrids were also constructed. They expect that their system could be used to gain important insight into particle–particle interactions.

To summarize, several important advances have been made in the controlled self-assembly of molecules and nanomaterials, attributable to surface functionalization and surface patterning strategies. Although it is difficult to draw a boundary line between these two strategies, both have contributed immensely to improvements in precision and resolution at the nanoscale. With the strong inspiration derived from biology and the use of programmable biomolecules for assembly, it can be expected that more and more complex structures of man-made materials at the nanoscale will become possible in the near future.

3. Fabrication of freestanding ultrathin films via self-assembly

Freestanding films are two-dimensional materials with minimal or no support. These materials, especially membranes (porous materials with permeability), have existed since prehistory since Nature has evolved their use in performing many complex functions in biological species. There has been a gradual increase in interest in freestanding films capable of performing various functions ranging from filtration to energy harvesting, and which might solve worldwide problems including access to safe drinking water and the global energy crisis. In this regard, freestanding ultrathin films have attracted attention due to their unique combination of mechanical properties such as lightweightness, robustness and flexibility [21–24]. These films possess nanoscale thickness across macroscopic dimensions, making them suitable for a broad range of applications including separations, sensing, flexible electronics, biomedicine and energy storage [24,25]. Top-down approaches, especially lithographic techniques, have been widely used for the fabrication of freestanding ultrathin films [26,27]. In spite of their success, these techniques are time consuming and require expensive tools. In addition, as these techniques approach their fundamental and technological limits, bottom-up approaches can overcome many of the above limitations and also provide better fabrication efficiency at the nanoscale/molecular level [1**].

The fabrication of freestanding ultrathin films by the bottom-up approach requires a one-dimensionally confined environment. The use of self-assembly techniques to fabricate freestanding ultrathin films has become more popular in the past few years and the available methods can be classified under three broad categories: (i) formation of thin film on a solid substrate followed by a lift-off process; (ii) formation of thin film at a fluid–fluid interface followed by direct extraction; (iii) formation of a freestanding film using a peripheral support by a drying mediated self-assembly process. These methods are schematically depicted in Fig. 3. Most of the above methods, in addition to other available methods such as filtration and blown-film extrusion, are discussed in detail by Luo and coworkers [6*]. Hence, we will show only some representative examples to illustrate the recent progresses in this field.

3.1. Formation using solid substrate

The most common method employed in the fabrication of freestanding films is to use a solid substrate. This can be accomplished by a variety of techniques such as LB transfer, LbL assembly, spin-coating, electrophoretic deposition and cross-linking of SAMs. Each of these techniques provides varying degrees of control over film

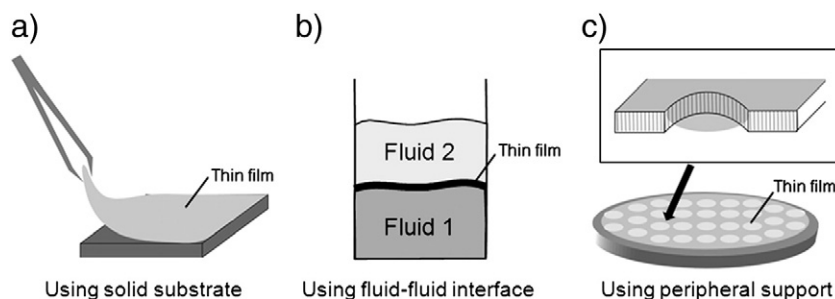


Fig. 3. Fabrication of freestanding ultrathin films; (a) formation using solid substrate and subsequent detachment; (b) formation using fluid–fluid interface; (c) formation using peripheral support.

thickness, composition and stability. Fabrication of a freestanding film using these approaches typically requires removal or transfer of formed film from the solid substrate, either by physical detachment or chemical treatment against a sacrificial layer. The conditions of the detachment process also vary between the different techniques, and depending on the severity could potentially compromise the structural integrity of the freestanding film.

One of the most important criteria in freestanding ultrathin films is the aspect ratio (size/thickness), i.e., large macroscopic lateral dimensions but nanometer-sized thickness. Kunitake and coworkers performed pioneering work in this area, wherein they fabricated giant nanomembranes having thicknesses of 1–100 nm and an aspect ratio of greater than one million [28*]. One of their approaches to fabricate giant nanomembranes involved spin coating of precursors onto sacrificial under layers, followed by detachment of the obtained freestanding film through dissolution of the sacrificial layers [29]. Using this approach, they prepared quasi-two-dimensional nanomembranes of organic–inorganic interpenetrated networks with unique combinations of unusual properties, namely macroscopic robustness, mechanical strength, high flexibility, optical transparency and homogeneity. Notably, these freestanding nanomembranes of macroscopic size can be used to seal large openings, strong enough to hold amounts of liquid 70,000 times heavier than their own weight, and flexible enough to reversibly pass through holes 30,000 times smaller than their own size. They also fabricated freestanding giant nanomembranes composed entirely of organic materials and a variety of resins including epoxy, melamine, phthalate or urethane by using the spin coating approach [30]. It is noteworthy that the nanomembranes based on epoxy resin were defect-free and possessed high electrical insulating behavior where the resistivity value remained essentially the same in comparison to the non-freestanding film.

A paradigm shift from conventional thinking comes about when we consider materials at the bulk and nano dimensions. This is especially true for freestanding ceramic nanofilms developed by Kunitake and coworkers [31]. Although ceramics are generally considered to be hard materials, these freestanding nanofilms were surprisingly soft and flexible. The softness of these nanofilms was attributed to their amorphous nature and ultrathin characteristics, leading to weak bonding interactions on the atomic and molecular scale. In addition, self-supporting metal oxide nanofilms as well as metal oxide–polymer composite thin films were fabricated elegantly by employing surface sol–gel processes [28*]. Furthermore, freestanding nanofilms of Pt and Pt–Pd alloy were prepared by a facile approach involving sputtering of metals onto a sacrificial polymer film, although these films were fragile and crack formation could not be avoided [32].

Self-assembly of block copolymers has been used to construct freestanding nanostructured thin films. Quémener and coworkers demonstrated the preparation of freestanding nanomaterials constructed from triblock copolymers involving polyethylene oxide,

polystyrene, and polyacrylonitrile [33]. The polymer film was prepared by spin coating onto a Si wafer and subsequently made into a freestanding film. The resulting material showed good mechanical properties without forming cracks under tension. They expect to use this film for membrane technological applications.

3.2. Formation using a fluid–fluid interface

A fluid–fluid interface can be used as a mobile two-dimensional platform for the assembly of freestanding films. The films formed at these interfaces can be directly extracted, thus avoiding any chemical or mechanical lift-off steps. Typically, a fluid–fluid interface can be classified as a liquid–liquid interface or a gas–liquid interface. At a liquid–liquid interface, the self-assembly of nanometer-sized objects is driven by the minimization of free energy, which includes contributions from thermal fluctuations and interfacial energy [29,30]. On the other hand, a gas–liquid interface, especially an air–water interface, has been widely used for the assembling of freestanding films from the constituent nanoscale building blocks. Most assemblies of molecules and nanomaterials at the air–water interface are subjected to cross-linking, either chemically or under light irradiation, in order to enhance the mechanical stability of the resulting freestanding films [34,35]. The self-assembly of nanoparticles at fluid–fluid interfaces is a fascinating and emerging area of research [36].

One of the recent techniques for fabricating well-ordered freestanding porous films directly from an air–water interface has been reported by Hao and coworkers [37]. They successfully fabricated highly ordered freestanding asymmetric honeycomb-type through-pore structures from nanocomposites consisting of polystyrene and gold nanoparticles at the air–water interface, using a one-step interfacial self-assembly method. Thus, a solution of dodecanethiol-stabilized gold nanoparticles and polystyrene in chloroform was spread onto a monolayer of dioctadecyldimethylammonium chloride formed at the air–water interface. The rapid evaporation of the solvent decreased the air–chloroform interfacial temperature below the dew point of the surface air, resulting in the formation of micrometer-sized water droplets on the chloroform surface. Coalescence of these water droplets could be prevented by the nanoparticles, since they stabilized the droplets causing their segregation at the chloroform–water interface. The water droplets then self-assembled into well-ordered hexagonal array that acted as a dynamic template for the formation of freestanding honeycomb films.

Another important approach employed in the fabrication of freestanding films is the floating self-assembly technique. Wang, Ge and coworkers reported a rapid and facile method for preparing freestanding colloidal crystal films from charged polystyrene spheres [38]. The polystyrene spheres were floated on the surface of liquid, which self-assembled into three-dimensionally ordered colloidal crystals over a large area. Freestanding film formation was facilitated by epichlorohydrin that worked as a cross-linking agent to enhance the mechanical stability. Their facile approach to fabricate

freestanding films can be used as an ideal template for the preparation of porous materials.

3.3. Formation using peripheral support

One of the fabrication methods of freestanding films is by using a peripheral support, for example, within a hole or a ring. It is not usually easy to obtain uniform two-dimensional film over a large area using this drying mediated self-assembly process because of the far-from-equilibrium effects, especially during the late stages of the dewetting process [6*]. These limitations can be overcome by employing the molding microdroplets method, wherein rational control over local nucleation and growth of film can be achieved by spatially regulating the dewetting process [39]. Furthermore, this spatial confinement of the drying mediated process can be performed within microholes to yield freestanding nanofilms at their ultimate thickness limit [40*]. In addition to nanoparticles and polymers, surfactant molecules can also be assembled into freestanding films within microholes upon evaporation of solvent. These self-standing surfactant films can be used as robust templates for the formation of freestanding inorganic thin films [6*].

It is now well-known that the properties exhibited by metal nanoparticles are drastically different from their corresponding bulk materials, especially due to quantum size effects [19]. Although freestanding nanoparticle membranes have been fabricated by spin-assisted assembly [41], cross-linking [42] and surfactant templating [43] techniques in the recent past, fabrication of highly ordered superlattices was challenging. However, this limitation has been recently overcome by two approaches independently reported by Jaeger and coworkers [44*] and Luo and coworkers [40*], as described below.

A simple and efficient approach involving the application of self-assembly at an air–water interface was used for the fabrication of freestanding two-dimensional arrays of close packed gold nanoparticles capped with dodecanethiol by Jaeger and coworkers [44*]. They fabricated circular holes with diameters ranging between 400 nm and 2 μm on a silicon nitride coated Si wafer using electron-beam lithography and reactive ion etching. Subsequently, compact and well-ordered nanoparticle monolayers were formed at the air–water interface when the nanoparticle suspension was spread onto a drop of water resting on the support, which was followed by lift-off and

drying (Fig. 4a). It is noteworthy that this approach does not make use of cross-linking of ligands attached to nanoparticles or embedding nanoparticles in a polymer matrix. Furthermore, these freestanding arrays revealed very interesting mechanical properties such as high elasticity (Young's modulus in the order of several GPa), coupled with exceptional robustness and resilience at high temperatures, all of which could be attributed to the confinement of ligands on the nanoparticle surfaces and interstices between the nanoparticles. The resulting freestanding arrays were stable in air over several days. However, the fraction of arrays that tore during fabrication with an increase in the diameter of the hole and the maximum diameter investigated was 2.2 μm . Despite the simplicity and efficiency of this approach, it still remains questionable whether or not freestanding nanoparticle arrays spanning a large area can be fabricated using this method.

A modified micro-hole based drying mediated self-assembly process, controlled by the use of DNA as dry ligand, was employed by Luo and coworkers to fabricate freestanding nanoparticle superlattice sheets [40*]. The main advantage of this approach over Jaeger's approach [44*] is the precise control of shapes of discrete freestanding superlattice sheets, wherein the sheets do not extend beyond the patterned boundaries and are confined within the micro-hole (Fig. 4b). In addition, they could also finely tailor the structural (inter-particle spacing) and functional (plasmonic and mechanical) properties by adjusting the length of DNA ligands. It is important to mention that these freestanding gold nanoparticle superlattice sheets were fabricated without the requirement of specific Watson–Crick base-pairing. Although they successfully fabricated freestanding highly ordered nanoparticle sheets at their ultimate thickness limit, obtaining large area (at least in the order of mm^2) is yet to be demonstrated.

Graphene, the two-dimensional carbon material, has gained a lot of interest in recent years [45] and its discoverer was also awarded the Nobel Prize in Physics for the year 2010. Freestanding graphene and graphene oxide films have immense potential in the fabrication of futuristic devices not only in the field of electronics, but also in the fields of sensor technology, optronics and so on [45]. Liu and Seo have recently developed a technique based on a centrifugal evaporation process to fabricate freestanding graphene oxide films from colloidal suspensions [46]. They were able to successfully fabricate uniform freestanding graphene oxide films of size up to 9 cm^2 and

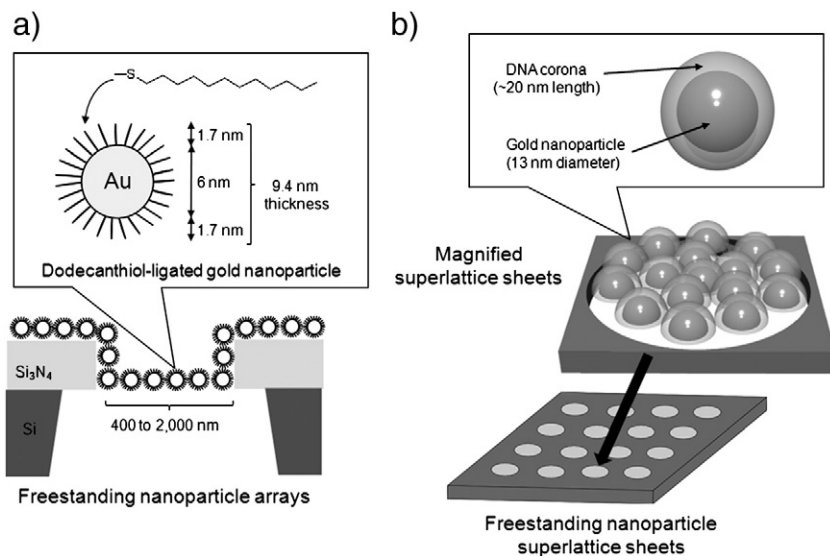


Fig. 4. Schematic diagrams of (a) freestanding ultrathin nanoparticle film and (b) drying mediated self-assembly process for the fabrication of freestanding nanoparticle superlattice sheets.

were also able to control the thickness of the film from 200 nm to 1 μm by varying the concentration of the colloidal suspension of graphene oxide and the evaporation temperature. In addition to possessing a smooth surface and high flexibility, the films were also highly transparent and stable.

To summarize briefly, several key problems in the fabrication of free-standing ultrathin films have been recently solved by self-assembly techniques. The resulting methods provide freestanding giant nanomembranes with thicknesses as low as 1 nm consisting of a variety of molecules and materials such as ceramics, metals, alloys, metal-inorganic nanoparticles and polymers. Furthermore, the obstacles that existed in the fabrication of well-ordered superlattices have been also overcome by new methods such as one-step interfacial self-assembly, floating self-assembly and micro-hole based self-assembly. Self-assembly of block copolymers, based on dynamic interaction between polymer blocks, continues to be used to construct advanced freestanding nanomembranes. Recent years have also witnessed the fabrication of technologically important materials such as graphene in the form of freestanding films. Still, in many of the cases, the issues regarding fragility and cracks need to be addressed. We anticipate that application of self-assembly concepts for the fabrication of freestanding films will increase in subsequent years.

4. Molecular assembly at dynamic interfaces

In the previous two sections, we have discussed the concepts and recent advances in manipulating thin film assemblies by modification of solid surfaces for supported films and fabrication of freestanding thin films through self-assembly. In this section, we will discuss one of the most important emerging fields, molecular self-assembly at dynamic interfaces, which enables us to directly manipulate molecular assembly by means of external stimuli such as mechanical compression. The most investigated dynamic interface is an air–water interface, which has long been recognized as an excellent medium for the assembly of several types of systems such as organic molecules, polymers, biopolymers, inorganic nanoparticles and so on. The widely used LB technology is an excellent example to illustrate the importance of dynamic interfaces for the preparation of two-dimensional molecular assemblies. Although the concept of Langmuir monolayers at the air–water interface has been known for many years, the recent work has resulted in the use of these monolayers for unusual tasks including molecular recognition and operation of molecular machines, in addition to the development of several techniques for their thorough characterization [4]. In this section, we will review the recent important achievements along with a short outlook into the future.

4.1. Molecular recognition at air–water interface

The air–water interface is known to promote molecular interactions such as hydrogen bonding, electrostatic, dipole–dipole and van der Waals interactions. These non-covalent interactions can be efficiently harnessed to induce molecular recognition, as demonstrated in biological molecules such as peptides, nucleotides and carbohydrates [47]. Ever since the realization of these capabilities, molecular recognition processes between monolayer components and guest molecules at the air–water interface have been a topic of extensive research, as illustrated in the review article by Leblanc [48].

Several researchers have investigated chiral recognition at the air–water interface, both within monolayer components and between monolayer and aqueous guests. Several studies have been published dealing with the formation of chiral structures from achiral components using the concepts of supramolecular chirality, and the dynamics of chiral selectivity induced by structure changes in the monolayer for selective molecular recognition [49–51]. Here, the very recent developments in this fast-growing field will be reviewed.

Berman and coworkers have reported on the enantioselective recognition between polydiacetylene nucleolipid monolayers and complementary oligonucleotides at the air–water interface [52]. They constructed a two-dimensional bio-synthetic hybrid system at the air–water interface composed of a polymerized diacetylene Langmuir film with nucleobase modified headgroups, capable of specifically binding complementary mononucleoside or oligonucleoside sequences. Using this system, enantioselective binding occurred as a result of surface induced asymmetry, which was caused by surface compression followed by polymerization, thereby demonstrating enantioselective interactions at dynamic interfaces.

Cyclodextrins are one of the important classes of host molecules that can selectively recognize and bind guest molecules. de Rossi and coworkers have shown the molecular recognition capabilities of monoacylated cyclodextrin derivatives to selectively bind aqueous guest molecules such as amino adamantane, phenolphthalein and fluorescent dye (prodan) at the air–water interface [53]. They reported that the cyclodextrin molecules adopted suitable conformations upon compression where the cavity was perpendicular against the water surface favoring intermolecular hydrogen bonding between two adjacent molecules. The conformational flexibility of these huge macrocyclic compounds at dynamic interfaces could be further exploited in the future to improve their molecular recognition capabilities.

One of the most recent advances in this field is the mechanical tuning of molecular recognition to discriminate the single-methyl-group difference between thymine and uracil, reported by our group [54^{**}]. Here, a novel cholesterol-armed triazacyclononane was used as a host molecule and was subjected to structural tuning by compression of its Langmuir monolayer on a water subphase containing lithium ions (Fig. 5a). It was found that the monolayer of the triazacyclononane host selectively recognized uracil over adenine (ca. 7 times based on the binding constant) and thymine (ca. 64 times) under optimized conditions ($[\text{LiCl}] = 10 \text{ mM}$ at surface pressure of 35 mN m^{-1}). The finding, mechanical tuning of the host molecule to recognize a specific guest molecule at dynamic interfaces, can be seen as a simple and practical method of molecular recognition, leading to the plausible conclusion that molecular recognition can be achieved through mechanical adaptation of simple host molecules within dynamic media, as an alternative to traditional strategies based on increasingly complex and inconvenient molecular design. It should be emphasized that this method is available even in cases of subtle molecular discrimination.

Kalinina and coworkers have also demonstrated the molecular recognition of uracil and adenine nucleobases by using Langmuir monolayers of metal complexes of amphiphilic cyclen [55]. They showed that the selective binding of uracil occurs in the presence of zinc ion in cyclic amine, which results from the formation of macrocyclic complex with metal ion followed by the coordination of uracil imide group to the metal complex, while the monolayer of zinc ion-cyclen complex was inactive to adenine. The authors envision that such monolayers of amphiphilic cyclen can be used as planar biomimetic models to study the function of active sites of transcription metalloproteins.

Not only has this field advanced in terms of pioneering experimental methodologies, but also on the theoretical side as well. Vollhardt and coworkers have reported a quantum chemical description of the thermodynamic characteristics of clustering of melamine-type amphiphiles at the air–water interface [56]. Amphiphilic melamine derivatives have been so far used as host components in monolayers and bilayers for interfacial molecular recognition of barbiturates since the pioneering work of Kunitake and coworkers [57]. They have used semiempirical PM3 methods to calculate the thermodynamic parameters of the formation of monomers, dimers, trimers and tetramers of amphiphilic melamine-type amphiphiles, wherein the parameters included enthalpy, entropy and Gibbs energy. They showed that both the alkyl chain length

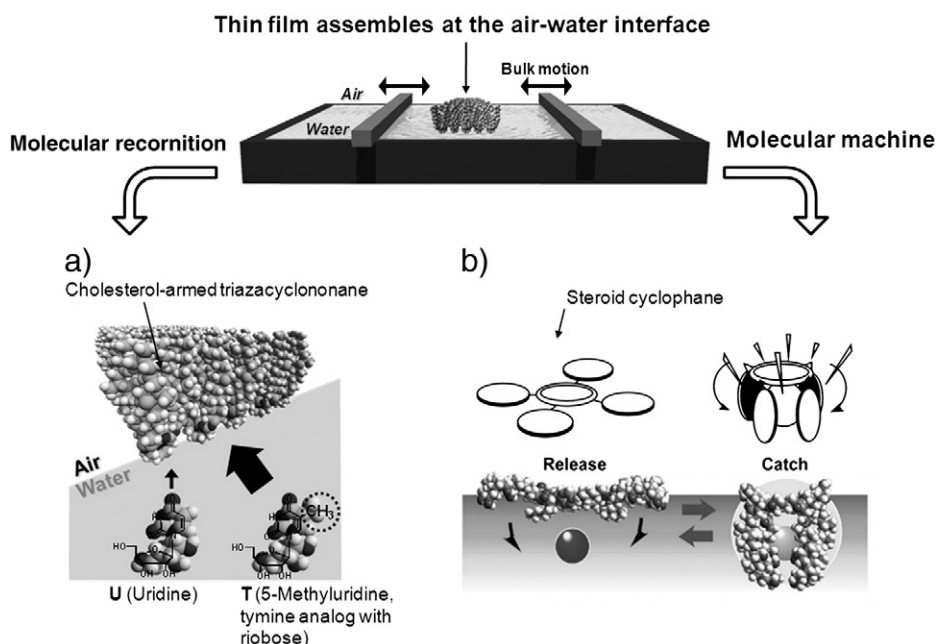


Fig. 5. Manipulation of molecular recognition and molecular machine at the air–water interface. (a) A single methyl discrimination of nucleobases by a cholesterol-armed triazacyclononane upon external mechanical stimuli. (b) Reversible capture and release of a guest molecule by using an armed host molecule (steroid cyclophane) through mechanical compression and expansion.

and hydrogen–hydrogen interactions play a crucial role in the clustering of melamine-type molecules at the air–water interface.

Based on the growth of this field, we anticipate that much more research works that exploit the possible recognition capabilities of molecules and their assemblies at dynamic interfaces will be available in the near future. However, by carefully manipulating the self-assembly processes at interfaces, even more sophisticated molecular recognition abilities can be induced in molecules that do not normally possess such properties.

4.2. Molecular machines at air–water interface

Molecular assemblies at fluid interfaces offer the possibility of dynamic conformational change and spatial rearrangement, which are unachievable in assemblies at constrained static interfaces. These conformational changes or the spatial rearrangements of molecular ensembles can be manipulated to construct so-called molecular machines, which are capable of performing several functions based on their response to external stimuli. It would be all the more interesting if the molecular assemblies could respond to macroscopic bulk external stimuli, which may enable the fabrication of practical mechanical devices for applications. Hence, the direct coupling of macroscopic and molecular motion is crucial and dynamic interface offers this feasibility. Basically, molecular ensembles at the air–water interface respond to changes in the applied surface pressure and can function as molecular machines, wherein the pressure change can actuate all the molecular machines in unison triggering their operation. That is to say, the molecular machines can be practically driven by macroscopic forces such as compression by hand.

Planar steroid cyclophanes belong to a particular class of molecules which can change conformational structure to form a dynamic cavity in response to an applied mechanical stimulus, especially when these molecules are embedded in monolayers at dynamic interfaces [47]. We first demonstrated the controllability of size of this dynamic cavity and intervals by manipulating the macroscopically applied surface pressure on an ensemble of steroid cyclophanes at the air–water interface, and proposed its use as a molecular actuator

[58*]. Naphthalene-type molecules are preferred guests of steroid cyclophane hosts because they are easily attracted to the central ring of the cyclophane and stabilized by the closed walls of the host. Furthermore, we demonstrated the reversible binding (catch and release) of an aqueous fluorescent naphthalene-type guest in a monolayer of a steroid cyclophane consisting of rigid 1,6,20,25-tetraaza [6.1.6.1] paracyclophane ring, connected to four steroid moieties (cholic acid) through flexible L-lysine spacers (Fig. 5b) [59*]. Tight capture of the guest molecule was achieved by compression of the monolayer to a high surface pressure, which was evidenced by the efficient enhancement in the fluorescence intensity due to the suppression of formation of the non-emissive states. In addition, the rapid motion of the reversible cavity formation by a high rate of compression and expansion of the monolayer resulted in better reproducibility in the fluorescence change, indicative of the dynamic capture and release of the guest molecule. These studies are a representative example of a practical molecular machine, whose operation can be controlled by macroscopic mechanical motion such as changes in surface pressure. Although applied by mechanically-operated moving barriers in the above study, the mechanical stimulus could equally be performed directly by hand. Therefore, this strategy can be regarded as “hand-operating (hand-operated) nanotechnology”, wherein a direct coupling between hand motion and molecular motion can be achieved [60*].

In yet another work, we employed the concept of hand-operating nanotechnology to produce a molecular machine at dynamic interface, which exploits molecular twisting to recognize enantioselectively the D- and L-forms of valine [61*]. Herein, we studied monolayers of cholesterol-armed cyclen sodium complex at the air–water interface and successfully demonstrated its ability to mechanically control the enantioselectivity for amino acid recognition. This molecular machine adopted two possible quadruple helicate structures and the helicity was influenced by the chirality of the side arms especially in ordered or aggregated states in a monolayer. Hence, the relative stability of diastereomeric guest molecules incorporated in the monolayer could be modulated by changing the helix structure, which in turn could be controlled by the compression and

expansion of the monolayer driven by bulk mechanical stimulus. This work will open a new methodology for the discrimination of chiral substances by hand.

All of these examples illustrate that manipulation of self-assembly of certain molecules at dynamic interfaces can lead to the construction of molecular machines capable of doing actuator operations in addition to performing molecular recognition. Furthermore, it is noteworthy to mention that all these manipulations can be performed by macroscopic bulk mechanical stimulus such as hand operation. Using these concepts, one day we might be able to touch the nanoscopic world directly with our hands and might be able directly to maneuver nano-objects!

4.3. Developments in characterization techniques

As the field of molecular assembly at dynamic interfaces progresses, there is an increasing need for the development of experimental techniques to characterize these fluid interfaces. Although several techniques encompassing the different methods in microscopy (e.g. Brewster angle microscopy), spectroscopy (e.g. optical, FT-IR, Raman spectroscopy) and scattering (e.g. light, X-ray, neutron scattering) exist for the characterization of monolayers at an air–water interface, these methods currently lack the sensitivity and spatial resolution to adequately investigate these systems. In this regard, we will review a few selected prominent developments for characterizing Langmuir monolayers at the air–water interface.

In several studies involving host–guest systems at dynamic interfaces, the concentration of guest molecules happens to be very low and sometimes becomes undetectable by any technique. Many researchers circumvent this problem by depositing multiple layers on solid substrates and characterize those using conventional techniques. However, it should be noted that the organization of molecules at solid interfaces is not exactly the same at the air–water interface. Hence, it is ideal to characterize the molecular assemblies directly at such dynamic interfaces, which may offer the possibility to observe the real-time structural evolution and dynamics of assembly process at these dynamic interfaces. In addition, combination of techniques which provide insights on a system from different perspectives is also of special importance.

Recently, Blasie and coworkers have developed a portable UV–vis spectrometer based technique for measuring absorbance and dichroism of Langmuir monolayers under *in situ* conditions, capable of obtaining reliable quantitative spectroscopic data from monolayer assemblies with absorbance as low as 1 mOD [62]. The spectrophotometer utilizes a standalone multipass sensor, which is placed in a

Langmuir trough and coupled with light source and spectrometer head via fiber optics. They studied several model systems including a variety of chromophores, fatty acid monolayers containing amphiphilic dyes and also a real system based on a synthetic peptide and a functional chromophore. Due to the portability and compact size of this spectrometer, they were able to couple this technique with X-ray scattering methods to investigate the same monolayer by using different techniques.

Another important technological development in the characterization of molecular assemblies at air–water interface was also reported by Blasie and coworkers, wherein a technique based on an interferometric approach was developed which substantially enhanced both the sensitivity and spatial resolution of the X-ray reflectivity method [63]. Despite its wide use, the relatively limited range of momentum transfer restricts the sensitivity and spatial resolution of X-ray reflectivity, both of which are needed for the thorough investigation of surface structure. They used a multilayer reference structure comprising Si and Ni layers (which have varying X-ray contrast) and positioned it close to the Langmuir monolayer on water surface without perturbing it, as in Fig. 6. The interference of X-ray reflected by this underlying reference structure was exploited to achieve high sensitivity and spatial resolution, in addition to obtaining a direct solution to the phase problem.

Time-resolved grazing incidence small angle X-ray scattering (GISAXS) is yet another remarkable technical improvement in this field. Terech and coworkers, in addition to developing this technique, have applied it to study the equilibrium and non-equilibrium states of organic/inorganic monolayers at liquid surfaces [64]. They compared the capabilities of this technique to the more classical X-ray specular reflectivity method, in addition to reporting the results of their investigations on time-resolved kinetics of lipid desorption from a monolayer, and structural evolution of biomembranes at low temperatures.

It is expected that in the future several advanced techniques will be developed to study self-assembly processes in great detail. This knowledge coupled with advancements in theoretical approaches based on computational modeling and energy optimization methods will enable us to more efficiently manipulate the molecular assemblies at the dynamic interfaces.

5. Conclusions

We have reviewed recent representative examples of manipulation of thin film assemblies, categorized into three basic classes, from the viewpoint of molecular self-assembly. This review illustrates several recent strategies toward manipulating thin film assemblies through surface functionalization and patterning of solid substrates, processing to form freestanding ultrathin films, and the dynamic nature of fluid–fluid interfaces. We strongly emphasize the concept of self-assembly at dynamic interfaces, which should continue to offer many new possibilities for the fabrication of effective molecular systems able to perform complex functions at the molecular level by responding to external mechanical triggers. We also foresee that dynamic interfaces might provide direct coupling between molecular motions and manual motions, as demonstrated in the final example, hand-operating (hand-operated) nanotechnology. It is likely that connecting thin film assemblies with molecular/nanometer size thickness with conventional macroscale stimuli, such as mechanical deformation, will become more and more important in developing nanodevices useful in our everyday lives, and could contribute to the eventual ubiquity of nanotechnology.

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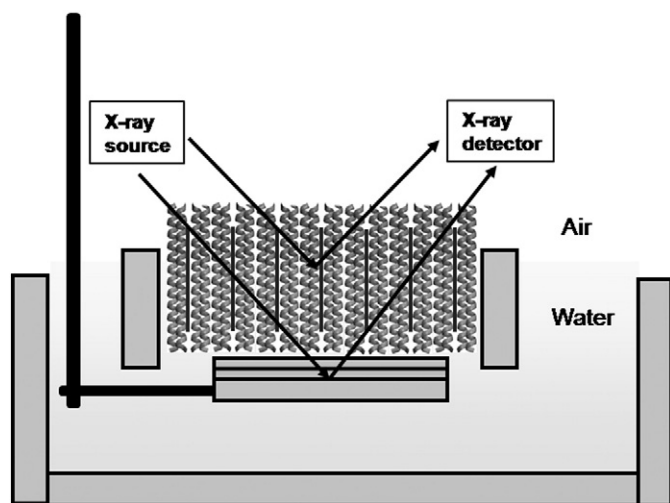


Fig. 6. Schematic representation of the interferometric approach to X-ray reflectivity to enhance its sensitivity and spatial resolution.

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