Assembly and Self-Assembly of Nanomembrane Materials—From 2D to 3D

Gaoshan Huang and Yongfeng Mei*

Nanoscience and nanotechnology offer great opportunities and challenges in both fundamental research and practical applications, which require precise control of building blocks with micro/nanoscale resolution in both individual and mass-production ways. The recent and intensive nanotechnology development gives birth to a new focus on nanomembrane materials, which are defined as structures with thickness limited to about one to several hundred nanometers and with much larger (typically at least two orders of magnitude larger, or even macroscopic scale) lateral dimensions. Nanomembranes can be readily processed in an accurate manner and integrated into functional devices and systems. In this Review, a nanotechnology perspective of nanomembranes is provided, with examples of science and applications in semiconductor, metal, insulator, polymer, and composite materials. Assisted assembly of nanomembranes leads to wrinkled/buckled geometries for flexible electronics and stacked structures for applications in photonics and thermoelectrics. Inspired by kirigami/origami, self-assembled 3D structures are constructed via strain engineering. Many advanced materials have begun to be explored in the format of nanomembranes and extend to biomimetic and 2D materials for various applications. Nanomembranes, as a new type of nanomaterials, allow nanotechnology in a controllable and precise way for practical applications and promise great potential for future nanorelated products.

1. Introduction

The concept of “nanotechnology” was first discussed in 1959 by renowned physicist Richard Feynman, and the term “nanotechnology” was first used by Norio Taniguchi in 1974.[1] The definition at the beginning was the technology used to synthesis via direct manipulation of atoms. With the rapid development of the integrated circuit industry in recent decades, the technologies used to fabricate and characterize devices with miniaturized feature size have attracted increasing interest and the scope of “nanotechnology” is widely extended. Nowadays, although an accurate definition is still absent, the nanoscale normally refers to the length scale between ~1 and ~100 nm.[2–4]

Nanomembranes and nanomaterials/nanostructures. Due to the small dimension, the structures should have high surface area to volume ratio, and the surface/interface states become important and even dominant compared to normal bulk materials.[5–7] In addition, the dimensional constraint may even give rise to quantum size effects, which can significantly change the energy spectrum of electrons and their behaviors.[6,8,9] As a result, these materials and structures show plenty of intriguing phenomena and extraordinary electronic, optical, thermal, mechanical, and chemical properties, and traditional disciplines could be reinterpreted. This provides a lot of fascinating research topics for fundamental researches. While for practical application, the new properties have already led to great potentials in numerous fields, including solar cells, photonic crystals, negative refractive index materials, light emitting devices, optical switching devices, quantum cascade lasers, nanolaminates, thermoelectric devices, etc.[10–17] The nanomaterials are actually 3D. However, since they have limited length scale in certain dimensionalities, the nanomaterials can be roughly categorized by their geometries into quasi-0D (0D, e.g., nanodot and nanoparticle, see transmission electron microscopy (TEM) image in Figure 1a),[18,19] quasi-1D (1D, e.g., nanowire and nanorod, see scanning electron microscopy (SEM) image in Figure 1b),[20,21] and quasi-2D (2D, e.g., nanosheet and nanoplate, see atomic force microscopy (AFM) image in Figure 1c1 and SEM image in Figure 1c2)[22–24] morphologies with unique features based on surface and structural characteristics. It is worth noting that the combination of these low-dimensional structures may lead to production of 3D structures with feature size in nanoscale via assembly or self-assembly processes. For example, Figure 1d1 shows the SEM image of PbS pine tree nanowires synthesized by chemical vapor deposition,[25] and Figure 1d2 shows 3D structure made by compressive buckling.[26] Various 3D structures may also be directly fabricated by micro/nanofabrication techniques like 3D printing or direct laser writing, and a typical example is presented in Figure 1d3.[27] As a step further, an interesting approach—so called 4D printing which relies on a combination...
of materials and geometry that can be controlled in space and time was recently developed.[26] Dynamically reconfigurable materials/structures with tunable functionality were produced.[28,29] As shown in Figure 1e, the printed bilayer architecture is encoded with localized swelling anisotropy that induces complex shape changes on immersion in water.[28] Smart materials and structures with the ability to respond to the external stimulations adaptively and dynamically are thus plausible, and their potential applications can be expected.[28–30]

Nanostructures and nanomaterials with different geometrical features have been intensively investigated in recent years. Especially, the researches concerning ultrathin 2D materials have broken out since 2004 with the first isolation and electrical characterization of graphene transistor reported by Novoselov et al.[23] Scientists pay much attention to 2D materials with thickness of just one or a few atomic layers and the number of related publications has increased rapidly. These ultrathin 2D materials like graphene and transition metal dichalcogenides are now usually made from naturally layered materials, that is, the van der Waals solids.[31–35] It is worth noting that although these 2D materials/structures are more “2D,” they still cannot represent those traditional 2D nanomaterials, and the related researches have been stimulated. Large Bohr radius of tens of nanometers for certain materials suggests that a much larger and diverse portfolio of 2D nanomaterials including nonlayered compounds may also possess interesting features and therefore can meet the specific requirements of individual components in various devices.[36,37]

The rapid development in 2D nanomaterials/ nanostructures gives birth to a new focus on nanomembranes, which are defined by us as structures with thickness limited to about one to several hundred nanometers and with much large (typically at least two orders of magnitude large, or even macroscopic scale) lateral dimensions. The nanomembrane structures are generally isolated from their environment on both sides (e.g., by air, vacuum, or a dissimilar deliberately introduced other material).[38] It is worth noting that the upper limit of the thickness is extended a little bit, because some unique physical properties like flexibility may also be obtained in thicker cases. In addition, as a field with rapid development, definition of the nanomembrane may vary a little in different literature,[24,39] and a widely accepted definition is currently unavailable. Therefore, one should notice that the structures called as, e.g., nanosheets, nanofilms, nanolayers, and nanoribbons in the literature may also be considered as nanomembranes according to the current definition. In fact, the nanomembranes have a feature size between the atomic scale and macroscopic scale in the vertical direction and they bridge the gap between nano and macro, since they have large lateral dimensions.[38] Interesting properties and amazing applications may thus be derived from this unique geometry.[24,36,38–44] In this review, we will summarize recent progresses in this field, especially the structures and devices made by (self-)assembling nanomembranes. The technologies adopted in fabricating (self-)assembled nanomembrane structures will first be introduced. The applications of assembled nanomembrane devices in many fields, e.g., electronics and photonics, will be discussed. The 3D micro/nanostructures formed by (self-)assembly of 2D nanomembranes will be the next focus. Finally, biomimetic nanomembranes and 2D materials in nanomembrane format will be reviewed. As a relatively new field with rapid development, it is impossible for us to include all the publications and progresses here in the review, but we will try to demonstrate those typical and inspiring results in selected aspects. We believe nanomembranes with controllable and precise fabrication approaches will become an attractive direction for nanorelated researches, and more application potentials will be explored in the future.

2. Perspective of Nanomembrane Technology

2.1. Nanomembrane Design

A considerable amount of researches have been devoted to investigate the growth and underneath mechanism of nanomaterials. In the case of nanomembranes, the thickness is crucial since this is the most important feature for nanomembranes. Vapor phase deposition is commonly used in producing nanomembrane structures. The examples are chemical vapor deposition,[45–58] physical vapor deposition,[51–55] atomic layer deposition,[56–59] and molecular beam epitaxy,[60–63] etc. In these approaches, source materials travel through reduced background
pressure in the chamber and condense on the substrate to form designed materials with or without chemical reactions. Many materials like semiconductor, metal, insulator, polymer, and composite materials have so far been deposited by these approaches in the form of nanomembrane with high quality and accurate thickness. Panel (i) in Figure 2a demonstrated a bird-view image of GaN nanomembrane synthesized by chemical vapor deposition. In addition, the strain status in the deposited nanomembrane can be easily tuned by changing the experimental parameters during deposition or by epitaxial growth of materials with different lattice constants. However, the vapor deposition normally requires special equipment and the cost is relatively high. Thus, fabrication in the liquid form can also be found in previous literature. Some materials (e.g., organic materials) can form a nanomembrane structure simply by normal spin-coating process or layer-by-layer assembly process. But in most cases, chemical reactions must be involved to synthesize the materials needed. One can find the nanomembranes fabricated by sol–gel method, hydrothermal/solvothermal synthesis, etc.

Besides these well-known approaches, researchers continuously develop new approaches on a case-dependent basis. For instance, Schrettl et al. used amphiphiles that contain hexayne segments as metastable carbon precursors and self-assembled these into ordered monolayers at the air/water interface. Subsequent carbonization by ultraviolet irradiation in ambient conditions resulted in the carbonization of the hexayne layer. Carbon nanomembranes prepared in this way exhibited a molecularly defined thickness of 1.9 nm, and a macroscopic lateral dimensions on the order of centimeters.

In order to obtain nanomembrane with large area especially for those nonlayered materials, one common strategy is to employ surfactant molecules or ions that are preferentially adsorbed on specific crystal facets, the growth of which is then retarded to form planar structure. By adopting a similar idea, Wang et al. prepared surfactant (e.g., sodium dodecyl sulfate or sodium oleylsulfate) monolayers which served as soft templates guiding the nucleation of designed ions. In this process (called as adaptive ionic layer epitaxy, see the inset of panel (ii) of Figure 2a), the packing density of surfactant monolayer adapts to the metal ions and guides the epitaxial growth of the nanomembrane. One to two nm thick, single-crystalline free-standing ZnO nanomembranes with sizes up to tens of micrometers were first synthesized at the water–air interface (panel (ii) of Figure 2a) and it was believed that this approach could also be applied to other materials. Obviously, the morphology of nanomembrane fabricated by this wet chemistry approach was significantly influenced by the chemicals used and therefore can be easily tuned.

In addition to assembling ions/atoms for nanomembranes, nanoparticles or nanowires may also be used as building blocks for the assembly process. Organization of these artificial “meta-atoms” represents an unconventional way to obtaining free-standing nanomembrane. The self-assembly of surface-decorated metal nanostructures at the air/water interface...
produced nanomembrane with thickness in nanometer scale while the lateral dimension in millimeter scale. The process can be further controlled by introducing DNA as a “dry ligand,” and therefore the structural and the functional properties of the freestanding were rationally controlled by adjusting DNA length. Specifically, this kind of nanomembranes demonstrated excellent robustness due to connection via ligands, and the Young’s moduli and spring constants varied with the length of ligand.

Nanomembranes may also be obtained by thinning the bulk materials to decrease the thickness. Different thinning methods have been developed for various materials systems. For layered materials, nanomembranes are obtained by well-known mechanical exfoliation (e.g., by scotch tape), where only one or a few layers are separated from the bulk. This method was first used to fabricate graphene monolayer and then extended to other layered materials. To improve the productivity of such kind of 2D structures, sonication exfoliation and chemical exfoliation were later introduced for certain layered materials.

A widely used method to fabricate inorganic nanomembranes especially those nonlayered single-crystal semiconductor nanomembranes is ion implantation, which produces “semiconductor on insulator” structures. Typically, in the case of Si, a buried high dose oxygen implantation is converted to silicon oxide by a high temperature annealing process, and the top Si layer (i.e., Si nanomembrane) is separated from the substrate. In order to improve the homogeneity and crystal quality of the top layer, a technology called as “Smart-Cut” was later invented, where hydrogen ions, instead of oxygen ions, were implanted to single crystal semiconductor wafers. The implantation of hydrogen ions and subsequent annealing partially break the covalent bond at certain position (depends on the implantation energy) to form a mechanically cleavable plane, and thus, various semiconductor nanomembranes were fabricated with large area, high quality, and low cost.

2.2. Releasing Process

The obtained nanomembranes normally need to be further handled for application purpose. One of the typical post-treatments is the patterning. Sophisticated structures with small dimension can be realized by a conventional lithography (photolithography or ebeam lithography) step which is compatible with traditional Si planar technology. Accompanied chemical etching or reactive ion etching should be used to transfer the pattern in resist formed in lithography to the nanomembrane. Occasionally, patterning simply by mechanical scratching may also be applied for a quick test. Another important post-treatment is releasing the nanomembranes, since in most cases the nanomembranes are closely attached to the substrate. The solution here is to insert a removable layer below the nanomembrane, which is commonly called as sacrificial layer and can be selectively removed typically by chemical etching while the nanomembrane is kept intact (see panel (i) in Figure 2a). The released nanomembranes can be transferred to other substrates (e.g., plastic and other flexible substrates) for device fabrication because high quality nanomembrane may not be directly grown on these substrates. Wet transfer process is simple and can be accomplished without special equipment. In a typical process, the released nanomembrane was transferred to water first (see the photograph in panel (i) of Figure 2b). The target substrate was then dipped into the water and the nanomembrane adhered to it through capillary action. However, if the nanomembrane needs to be transferred accurately to certain position, an improved dry transfer process should be engaged and Roger and co-workers thus developed a “transfer printing” process. The process is accomplished by using a microstructured elastomeric stamp (polydimethylsiloxane, PDMS, in most cases) to selectively “pick-up” patterned nanomembranes or even devices from a source substrate (panel...
(ii) of Figure 2b) and then "place"/"print" structures onto a target substrate.\textsuperscript{[108–112]} It is worth noting that the details of transfer printing may slightly vary in different experimental works. In this dry transfer process, the stamps are designed to transfer hundreds to thousands of discrete pieces in a single pick-up and print operations, and therefore the process is massively parallel.\textsuperscript{[113]} One may notice that the transfer relies on the different adhesion forces at the interfaces, and for an effective transfer the magnitudes of the adhesion forces should be in the following order: source substrate/nanomembrane < stamp/nanomembrane < target substrate/nanomembrane. This requirement can be satisfied by handling the surfaces using chemical treatment\textsuperscript{[114,115]} or heating treatment,\textsuperscript{[116]} introducing fine surface structure,\textsuperscript{[108]} as well as engaging kinetic control of adhesion.\textsuperscript{[109,117]} Transfer printer or similar equipment may also be used to improve the accuracy of the position control. A comprehensive review concerning transfer printing process and corresponding device fabrication was previously published by Carlson et al.\textsuperscript{[118]} In addition to the basic rules for transfer printing, special consideration may be incorporated to produce nanomembranes with sophisticated structures. For example, patterning and transferring processes can be finished simultaneously in one step. By utilizing a modified transfer printing process with edge cutting effect, the semiconductor nanomembranes can be patterned into nanoribbons while be transferred to target substrate at the same time.\textsuperscript{[109]} The edge cutting led to transfer of nanoribbon with complex geometry.\textsuperscript{[109]} Since the width of the nanoribbon is determined by the time of under etching, this process is capable of producing nanoribbon at specific position with the width exceeding the resolution limit of photolithography, which provides great convenience for device fabrication.\textsuperscript{[109]}

2.3. Construction Method

In addition, many 3D micro/nanostructures can be constructed by using the nanomembranes as starting materials or building blocks. It is worth noting that the stiffness of the nanomembrane is significantly reduced due to remarkably decreased thickness, although the mechanical parameters, such as elastic constant and modulus, do not change.\textsuperscript{[106]} The flexibility of the nanomembranes thus makes them suitable for the construction processes. The construction processes normally include assembly and self-assembly approaches, and the ability of these techniques in constructing sophisticated 3D structures with possible device applications is briefly demonstrated in Figure 2c. As shown in panel (i) of Figure 2c, nanomembranes are assembled into a multilayer stack with translational and rotational increments by tuning the adhesion at the interfaces.\textsuperscript{[108]} On the other hand, if the internal strain and/or thickness of the nanomembrane are regulated, unique 3D structures can be construct via self-assembly process. Panel (ii) of Figure 2c shows the morphology of a self-rolled tube-in-tube structure by thinning nanomembrane locally before releasing and rolling.\textsuperscript{[109]} The methodologies and applications of these interesting 3D structures constructed by assembly and self-assembly processes will be discussed in detail respectively in the following sections, Sections 3 and 4.

We would like to stress that as a rapidly developing area, many new nanomembrane technologies emerge, and thus we cannot list all of them here. The exploration of new technologies and the improvement of the existed ones both aim to expanding applicable materials and reducing the handling difficulties and the cost. Technology associated with certain materials or material systems may also be paid attention. Moreover, constructing 3D structures in a smart manner and with better controllability is important. The innovation will be continuously motivated by novel properties and applications of nanomembranes and corresponding 3D structures in many fields. Some of examples will be discussed in the following sections.

3. Assembling Nanomembranes for Novel Electronics and Photonics

Various electrical and optical devices based on nanomembranes of different materials have so far been produced due to their unique properties.\textsuperscript{[53–55,119–126]} Especially, the nanomembranes are mechanically soft compared with the bulk counterpart because of the small thickness, and therefore, they can be easily assembled into 3D geometries for application purpose.\textsuperscript{[106,120]} The nanomembranes with wrinkles or buckles can accommodate vast strain, and thus paving the way for their use in wearable, stretchable, or curvilinear devices.\textsuperscript{[127–129]}

3.1. Assembled Nanomembranes for Novel Electronics and Photonics

Devices fabricated by assembling nanomembranes using aforementioned technologies like transfer printing were previously reported. A diversity of material classes with a wide range of geometries and configurations have been explored so far. In particular, nanomembrane devices can be assembled on target substrate to achieve heterogeneous integration in vertical direction. With the help of the rapid technical development in this area, researchers now can assemble more complicated 3D devices or even systems by vertically stacking the nanomembranes. This is meaningful because the high quality materials may not be able to directly grow on target substrate or the target substrate cannot survive the device fabrication process. For example, due to the high carrier mobility, high performance n- and p-type III–V metal-oxide-semiconductor field-effect transistors (MOSFETs) were respectively demonstrated by using As-based and Sb-based semiconductor materials as channels.\textsuperscript{[130,131]} Researchers therefore hope to produce III–V complementary MOS (CMOS) circuits on Si wafers due to the well-established process technology. A two-step transfer process was used to assemble InAs and InGaSb nanomembranes on one Si/SiO\textsubscript{2} substrate and a top gate CMOS inverter was obtained.\textsuperscript{[112]} Panels (j) and (ii) of Figure 3a show the diagram and SEM image of the device. Electrical characterization demonstrated that electron mobility can reach 1190 cm\textsuperscript{2} V\textsuperscript{−1} s\textsuperscript{−1} in n-MOSFET while hole mobility can reach 370 cm\textsuperscript{2} V\textsuperscript{−1} s\textsuperscript{−1} in p-MOSFET, indicating the high carrier mobilities were successfully preserved in nanomembrane structure. The performance of the inverter was characterized and the results...
Figure 3. (a) MOSFET devices fabricated by transfer printing of III–V compound semiconductor nanomembranes on Si/SiO$_2$ substrate. (i) Schematic diagram of the devices. (ii) Optical microscopy image of the devices. (iii) Inverter gain dependence on the input voltage. Adapted with permission.[132] Copyright 2012, American Chemical Society. (b) Assembled VCSEL by transfer printing. (i) Device structure. (ii) SEM image of a device, showing an InGaAsP quantum well layer sandwiched between top and bottom Si nanomembranes. (iii) Measured spectral outputs of the VCSEL at four pump power levels: below (1), at (2), and above (3 and 4) threshold. Inset: far-field image above threshold. Adapted with permission.[136] Copyright 2012, Macmillan Publishers Limited. (c) Assembled wavelength-tunable entangled photon source. (i) Schematic of the cross section of a device. (ii) Optical microscopy image of the device. The center region is a bonded QD-containing nanomembrane. (iii) Performance of a typical device. Adapted under the terms of the Creative Commons Attribution 4.0 International License.[138] Copyright 2016, Nature Publishing Group. (d) Assembled electrophysiological sensing system on flexible substrate. (i) A photograph of a completed capacitively coupled flexible sensing system with 396 nodes in a slightly bent state. The inset shows a magnified view of a few nodes. (ii) A photograph of a flexible sensing electronic system on a Langendorff-perfused rabbit heart. (iii) Representative voltage data obtained by the sensing system. Adapted with permission.[142] Copyright 2017, Macmillan Publishers Limited.
are presented in panel (iii) of Figure 3a. One can see that a gain of greater than 11 is obtained at $V_{DD} = 0.5$ V, which gradually improves with $V_{DD}$. By connecting more MOSFET on the same substrate, more logic operations can be realized. It is worth noting that electronic devices can directly be produced in a transferring and assembling process, even without utilizing those steps commonly used in semiconductor industry. As demonstrated in the work of Guo et al., a p-type Si nanomembrane and a n-type Ge nanomembrane were transferred in subsequent to form a vertical van der Waals heterojunction, and good rectifying behavior from this assembled pn junction was observed.

The assembly of nanomembranes with unique physical properties also have application potentials in photonics and optoelectronics. The transfer printing process provides the possibility of assembling nanomembrane into novel 3D stack structures for optical applications. Panel (i) of Figure 3b shows a diagram of a vertical-cavity surface-emitting laser (VCSEL) device with stacked nanomembranes. A transferred III–V InGaAsP quantum well active layer is sandwiched between two silicon photonic-crystal Fano resonance nanomembrane reflectors, as shown in the SEM image in panel (ii) of Figure 3b. The use of nanomembrane reflectors allows the laser device to be built directly on silicon substrates but with much reduced thickness. The simulation demonstrated a confinement factor of 6% which is similar to the values obtained from the devices with conventional thick distributed Bragg reflectors. The threshold pump power was found to be $\approx 8$ mW, or $0.32$ kW cm$^{-2}$, and the measured spectral linewidths reduced from 30 nm below threshold to 0.6–0.8 nm above threshold. The corresponding measured spectra are shown in panel (iii) of Figure 3b for pump power below, at, and above threshold. The inset is a measured far-field image for the VCSEL device biased above threshold (spectrum 4), with collimated circular single-mode output. Experimental results demonstrate that such a 3D laser device has a much tighter field distribution, with reduced energy penetration depth and device dimensions. Moreover, the fabrication technique of stacking nanomembranes enables the creation of many high-performance photonic devices on different substrates, as well as a planar structure that allows much simpler integration schemes.

It is also possible to assemble a combination of devices with different functions. Recently, researchers produced a unique combination of the monolithically integrated microelectromechanical system and the semiconductor quantum dot-based quantum light source, which provided fresh opportunities for on-chip quantum photonic applications. Panel (i) of Figure 3c shows the schematic of the cross section of a device. The piezoelectric $(1-x)\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$–x$\text{PbTiO}_3$ (PMN-PT) layer as actuator was bonded on a Si substrate, and quantum dots containing GaAs nanomembrane were then transferred onto the top of the device. The top view of the device is displayed in panel (ii) of Figure 3c. When applying voltage to the electric contacts, the PMN-PT layer expanded or contracted in-plane and therefore exerted quasi-uniaxial stresses to the quantum dots. Experimental results demonstrate that the excitation emission is shifted over a large range (up to 10 nm in wavelength or 12 meV in energy), as shown in panel (iii) of Figure 3c. This vertically assembled device is highly integrated, and the small thickness of the nanomembrane reduces the voltage burden on the integrated device from hundreds or thousands of volts (necessary for bulk) to several volts.

The modern electronic systems are essentially fabricated on flat rigid semiconductor substrates, which limits their application in biology since most biological applications involve soft and curved surfaces. The assembly approach based on transfer printing thus provides the possibility of producing electronic system on flexible substrate, and thus the system can intimately contact the soft and curvilinear surfaces of the tissues or organs. A typical example is presented in Figure 3d. The overall system consists of 396 multiplexed capacitive sensors (18 columns, 22 rows), each with dimensions of $500 \times 500 \text{ m}^2$. The system distributed uniformly over a total area of $9.5 \times 11.5$ mm$^2$ was first fabricated on Si-on-insulator and then transferred to a flexible substrate (panel (i) of Figure 3d). Cardiac mapping experiments involve recording of unipolar voltage signals from all 396 nodes on multiple ex vivo Langendorff perfused rabbit hearts. As shown in panel (ii) of Figure 3d, the device conformally covers the curvilinear surface of the heart. High-definition electrophysiology mapping from all sensors is displayed in panel (iii) of Figure 3d. It is worth noting that this technology platform is important not only for cardiac applications, but also for electrophysiological sensing of other organ systems, and for use as implants in live animal models and multiple functions can also be incorporated. In addition, if biodegradable materials are used, it is possible to obtain electronic systems which can operate in a stable, high-performance manner for a desired time and then degrade and disappear completely as in the case of transient electronics.

### 3.2. Waved Nanomembranes for Flexible and Wearable Electronics

In inorganic flexible electronics, the bendability of the flexible electrical devices on elastic substrates can be improved if the neutral mechanical plane, which defines the position through the thickness of the structure where strains are zero for arbitrarily curvature radius, lies in the device layer. In order to achieve even good stretchability, researchers used waved nanomembrane as interconnection of the circuits or even as active layer of the devices. The waved structures are commonly fabricated by applying compressive forces on the printed nanomembrane, leading to the formation of wavy geometry. The corresponding flexible systems therefore normally combine high-quality nanomembrane devices in “wavy” structural layout with elastomeric substrates. In such a case, the devices are even stretchable and bendable while high electrical performance remains because the neutral mechanical plane is located at the proper position. This strategy is currently applicable to many highly integrated systems with diverse classes of electronic materials which are intrinsic brittle and fragile. The fabricated devices have great potential in safety and healthcare monitoring, consumer electronics, and electronic skin devices, etc.

The optical micrograph in panel (i) of Figure 4a demonstrates a printed Si CMOS inverter with wavy geometry, which was
produced with prestrain $\varepsilon_{\text{pre}} = 2.7\%$. The wavy nanomembrane has complex layout associated with nonlinear buckles. It was noticed that the waves first formed in the regions of smallest flexural rigidity and extends with the increase of prestrain.

The phenomenon was investigated theoretically with the help of finite element analyses. When external forces were applied to the device, the amplitudes and periods of waves that lie along the direction of applied force decrease and increase, respectively, to accommodate the resulting strains ($\varepsilon_{\text{appl}}$), while Poisson effect causes compression in the orthogonal direction, leading to increases and decreases in the amplitudes and periods of waves along this direction, respectively.

Electrical characterizations indicate that the devices work well under such externally applied strains: the mobilities are 290 and 140 cm$^2$/V·s for electron in the n-channel and hole in p-channel devices, respectively, to accommodate the resulting strains ($\varepsilon_{\text{appl}}$), while Poisson effect causes compression in the orthogonal direction, leading to increases and decreases in the amplitudes and periods of waves along this direction, respectively.

The observed fluctuation was ascribed to the change in electron and hole mobilities. The concept of increasing stretchability by fabricating device with wavy geometry can be expanded both in materials and functionalities of the devices. Guo et al. prepared a photodetector based on single-crystal Ge nanomembrane with 1D buckles. The current–voltage ($I$–$V$) characteristics of the wrinkled photodetector with different bending strains were measured and variations can be barely observed when the strain is varied from 0% to 8.6%, illustrating good flexibility of the device.

Figure 4b demonstrates a novel photodetector device based on a Si nanomembrane wrapping on a single-mode optical fiber. Here, the device is constructed by assembling Si nanomembrane on a 20 cm long fiber which guides light. As shown in panel (i) of Figure 4b, the Si nanomembrane contacts with silver paste to form metal–semiconductor–metal photodetector and the channel length is $\approx 100$ m. The small thickness of the Si nanomembrane and the wavy/wrinkle structure therein guaranteed very good flexibility and bending of the fiber cannot produce observable crack. It was noticed that when the fiber was bent, some portion of light was likely to leak from core to the outer surface and then absorbed by the device, which can be detected.

Panel (ii) of Figure 4b shows ratio of photocurrent and dark current varying with the curvature of fiber, and the calculated bending loss caused by curvature is also showed for comparison. A good agreement indicates that light leakage is absorbed by the Si nanomembrane, leading to sensitive photodetection.

Piezoelectric nanomembranes were also found to benefit from the wavy geometry. Panel (i) of Figure 4c shows lead zirconate titanate (PZT, Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$) nanoribbons with a wavy structure, and the PZT nanoribbons thus can sustain large tensile strains. Experimentally, the current wavy structure can accommodate order-of-magnitude larger strain compared to the flat counterpart. In addition, it was noticed that the strain can significantly affect the piezoelectric response due to perovskite domain reorientation or polarization and an up
to 70% increase in piezoelectric response was obtained in the waved PZT nanomembrane.\cite{164} Since the waved nanomembrane demonstrated good stretchability, a simple energy conversion device can be fabricated by repeatedly stretching and releasing the waved nanomembrane. The current signal was recorded and is shown in panel (ii) of Figure 4c. Successful energy harvesting behavior is observed.\cite{162}

Recently, researchers have assembled waved magnetic sensor after transferring the entire device to elastic substrate.\cite{165-167} The morphology of the sensor made from [Co/Cu]_{50} multilayer nanomembrane after formation of wavy structure is displayed in panel (i) of Figure 4d. Here, the working principle of the sensor relies on the giant magnetoresistive (GMR) effect. The waved GMR device revealed an increased saturation field, which was attributed to the out-of-plane components of the magnetization at the sidewalls of the wrinkles.\cite{166} The stretchability of the waved device was tested by using a stretching stage shown in panel (ii) of Figure 4d (inset). The GMR magnitude and the sensor resistance as a function of the applied tensile strain was then recorded. As shown in panel (ii) of Figure 4d, both values are subjected to only small changes up to an elongation of 30%. The maintained resistance further proved that only a very limited number of cracks are induced during stretching test.\cite{166}

4. Nanomembrane Origami

As shown in Figure 2c, 3D micro/nanostructures can be constructed by an out-of-plane self-assembly process. Inspired by ancient paper arts (e.g., origami and kirigami), researchers established concepts for realizing more complex 3D structures from nanomembranes.\cite{168} Origami, a word originating from Japanese, refers to folding (“ori-”) of paper (“gami-“), while kirigami, refers to cutting (“kiri-“) of paper.\cite{169} Over 200 different 3D structures have been demonstrated by rolling, cutting, bending, and folding the nanomembranes.\cite{170-172} The structures were constructed by manipulating the strains in the nanomembranes and then unique 3D devices including microelectronic circuits, sensors, antennas, metamaterials, robotic, etc., have been obtained via self-assembly.\cite{168}

4.1. Rolled-Up Nanomembranes for 3D Devices

From the viewpoint of energy minimization, the formation of those self-assembled structure can reduce the total elastic energy.\cite{106,120,173,174} Specifically, if large vertical strain gradient exists in the nanomembrane, it will make the nanomembrane bend or roll into a curved structure.\cite{104,105} Since it was invented about 16 years ago, many microtubular or nanotubular structures from various materials have been fabricated by this so-called rolled-up technology. Previous investigations demonstrated that the strain gradient can be experimentally introduced by utilizing lattice mismatch, altering parameters during deposition of nanomembrane, fabricating nanoparticles with surface tension, etc.\cite{18,38,175-177} The rolling direction can be controlled by experimental parameters and surface structures.\cite{103,178,179} Meanwhile, the diameter of the tubular structure is determined by the strain gradient and mechanical property of the material and thus can be tuned correspondingly.\cite{174} The rolled-up technology has made many 3D structures with cylindrical symmetry from a lot of materials and material combinations. Detailed mechanical properties of such 3D structures have been summarized in our previous review.\cite{173} These 3D structures combine the excellent properties of the constitutive materials with the unique geometries and thus possess novel features and potential applications in, e.g., electronics, electromagnetic waves, biology, robotics, and energy storage devices,\cite{38,180-182} and a few typical examples are presented as following.

With the increasing demand on power-supply in electric vehicles and large-scale stationary grid, high performance energy storage devices with larger energy density are urgently needed.\cite{183} However, many electrode materials suffer from rapid capacity degradation due to large volume variation during the charging/discharging process.\cite{184} The rolled-up structure was found to play a structural buffering role in minimizing the mechanical stress induced by the volume change process.\cite{185} The rolling process results in a significantly reduced intrinsic strain due to energy minimization, which can further improve capacity and cycling performance.\cite{185} By using this concept, researchers prepared rolled-up nanomembranes from various materials and used them as anode for Li-ion batteries.\cite{185-188} Panel (i) of Figure 5a shows the diagram of rolled-up C/Si/C trilayer nanomembrane. Here, the Si layer works as the active material for lithium ion storage, while the C layer serves as the supporting layer because of its high stability and excellent conductivity. The rolled-up geometry exhibited synergistic properties and superior electrochemical performance when used as anodes. As shown in panel (ii) of Figure 5a, stable rate capability of the anode is observed. The capacity gradually decreases with increasing current density from a low current rate of 0.1 A g^{-1} to a high current rate of 25 A g^{-1} and the capacity reversibly recovers to \approx 1000 mA h g^{-1} once the current rate goes back to 0.5 A g^{-1}.\cite{185} In addition to the improved stability, the energy storage device based on rolled-up nanomembrane also has the advantages of miniaturization of the volume and reduction of the footprint area.\cite{189}

The microtubes made from rolled-up nanomembranes were previous used as optical microcavities, where optical resonance can be obtained.\cite{38,190-194} The microtubular cavity actually provides 3D confinement of the light: the ring-like cross section is a whispering-gallery type cavity while the propagation of light along the axis direction produces axial mode, like the case in Fabry–Perot cavity.\cite{43} For a rolled-up microtube with diameter of \approx 20 \mu m made from nanocrystalline diamond nanomembrane (panel (i) of Figure 5b), the photoluminescence spectrum (red line in panel (ii) of Figure 5b) shows an obvious intensity modulation due to emitted light from color center coupled to the whispering gallery modes of the microtube.\cite{49} The quality-factor of the microtube is determined to be more than one thousand and the enhancement in the photoluminescence compared with flat nanomembrane was attributed to the light-trapping effect in the tubular geometry.\cite{49} Detailed characterization demonstrated that the wavelength and the polarization of optical resonance were significantly influenced by the geometrical features of rolled-up nanomembrane.\cite{195-197} The coupling effect between the resonance in the cavity and
a nearby object or surface plasmon from nanostructures made from noble metal has recently attracted increasing interest,[196–200] and the stack of nanomembranes during rolling process may be further used to architect 3D metamaterials.[201,202] Moreover, the evanescent interaction between the optical resonant mode and the surrounding medium near the tube wall (both inner and outer regions) leads to shift of the resonant wavelength and thus sensing applications can be achieved without any labelling processes.[203–205] The sensitivity can be as high as 880 nm per RIU.[206]

In the radio frequency region, inductors are essential components of radio frequency integrated circuits. However, the normal on-chip 2D inductors have large footprint and corresponding parasitic coupling capacitance and ohmic loss from the substrate lead to low quality-factor and resonance frequency.[207] Researchers thus designed on-chip inductor based on rolled-up technology. As shown in panel (i) of Figure 5c, metal stripes are rolled together with the SiN_x nanomembrane to form 3D multiple-turn spirals.[208] Shown in panel (ii) of Figure 5c is the effect of the number of rotations and the number of lateral unit cells on the total effective inductance L_{e_total} as a function of operating frequency. Large inductance can be obtained by increasing the number of rotations in each cell or connecting more cells in series.[208] The unique rolled-up 3D structure contributed directly to better confining the electromagnetic field and therefore enhanced the magnetic energy storage, leading to high inductance with smaller footprint and reduced substrate parasitic capacitance.[208,209]

The metal stripes rolled with nanomembrane may also be used to transmit electrical signals and thus, complex 3D electrical devices can be obtained.[210–212] The electrical device may be further incorporated with microfluidic functions to achieve a multifunctional sensor. Panel (i) of Figure 5d shows such a biosensor device based on rolled-up nanomembrane. Its performance (characterized by electrochemical impedance spectroscopy) is demonstrated in panel (ii) of Figure 5d, where performance of planar device is also shown for comparison. For the planar device, impedance value increases with increasing DNA concentration, whereas for the rolled-up device impedance value decreases.[210] The charge transfer resistance R_{CT} is very sensitive to the variation of DNA concentration in the am–pm range for rolled-up device, while the planar device is sensitive only in the pm range (panel (ii) of Figure 5d).

Recently, the development of thermoelectric devices with the potential for efficient energy conversion has attracted increasing interest. However, the delicate interplay between the electrical and thermal conductivity makes it difficult to optimize the thermoelectric performance of the structures.[213] It was found in previous literature that the cross-plane thermal conductivity of a layer is usually more suppressed compared to the in-plane thermal conductivity.[214] Therefore, in order to further reduce the thermal conductivity, researchers fabricated rolled-up nanomembrane and compressed the rolling structure to create a 3D stack with a large number of mechanically joined interfaces between nanomembranes with entirely different materials.[215,216] A substantial thermal transport reduction of two orders of magnitude was achieved in such structure.[213] The thermal coupling between different layers even caused the in-plane thermal conductivity decrease with the increase of the number of stacked nanomembranes.[215] The convenience in materials selection in this process provides possibility of producing stack with reduced thermal conductivity and high cross-plane electrical conductivity at the same time.[216]
4.2. Nanomembranes Origami/Kirigami for Smart Devices

Generally, compressive buckling is used to create deterministic assembly of these 3D structures.\[179\] In a typical process, the nanomembrane was first patterned into designed structure like nanoribbon by conventional photolithography and etching. The patterned structure was transferred to a water soluble tape to expose the backside surface. The surface chemical treatments (e.g., ultraviolet/ozone treatments)\[217\] were used to introduce hydroxy group to the certain bonding sites (i.e., anchors) of backside surface with the help of lithography. Then, the patterned nanomembrane was finally transferred to a tensilely prestrained silicone elastomer, whose surface was also chemically functionalized with hydroxy group. The covalent linkage at the bonding sites thus led to strong adhesion, and the bonding sites were fixed with the elastomer. Releasing the prestrain of the elastomer returned the elastomer to its original shape, which imparted large compressive force onto the nanomembrane. This, consequently, induced motions at the nonbonded regions, and complex 3D structures can be obtained by this self-assembling process.\[26,170,218\] It is worth noting that chemical treatments of the surface may not be a precondition for sufficient adhesion although the van der Waals force is relatively weak compared to covalent linkage. Some experiment work demonstrated the possibility of producing complex 3D structures without surface chemical treatment.\[219\] A typical 3D helical structure fabricated by this self-assembly process, as an example, is shown in Figure 6a. Experimental observations proved that during the self-assembly, in-plane bending is energetically unfavorable compared with out-of-plane bending or twisting, and therefore translational motion and out-of-plane bending or twisting were dominant in self-assembly.\[26\] In addition, the principle of the lowest energy can make the final 3D structure deterministic even for 2D nanomembrane with complex layout.\[26\]

If the patterned structure has relatively large lateral size, the lateral constraint during the bending process should be taken into consideration.\[170\] The in-plane stretching and out-of-plane bending may coexist in the self-assembling process. This may lead to localized stress concentrators of high strain energy that causes mechanical failure. In addition, for structure with large lateral size, the surface stiction induced by van der Waals may hinder the out-of-plane buckling.\[170\] Strain relief concepts inspired by kirigami can avoid these limitations. Introduction of cuts and slits in a precise manner (by, e.g., photolithography and etching) can dramatically reduce local strain concentration during compression, and a wide range of structures were obtained.\[102\] The results in Figure 6b present an example of self-assembly process of producing 3D structure from 2D nanomembrane, where a cross-cut pattern divides a large square into four smaller ones. Self-assembly thus forms a curved pyramidal structure. The simulation result indicated that the peak value of the strain in such kirigami-like structures was relatively small (e.g., below the fracture thresholds), owing to the stress-reducing effects of the cuts that formed the narrow hinges between the sides.\[103\] Obviously, the cuts played critical roles in defining the final 3D geometries, and their locations should (i) eliminate localized deformations and (ii) avoid any possible self-locking of different subcomponents.\[102\]

The self-assembly of the above 3D structures relies on global bending with smoothly varying levels of curvature. However, many desired 3D structures demand spatial localization of the bending, as in the case of origami. Engineered variation in thickness was found to be able to guide folding deformation at specific locations and thus provided such capability.\[220–223\] Simulation of the self-assembly process proved that when the thickness ratio was relatively small (e.g., <1/3), the thick regions underwent negligible deformation while the thin ones accommodated the compression via folding, and the maximum strains occured at these regions (so-called crease).\[220\] Reductions in the crease thickness and increases in the width can reduce the maximum strains in order to avoid fracture. Figure 6c demonstrates an example of origami-inspired 3D geometries through bidirectional folding.\[220\] In the 2D layout, four triangular structures connect at the center with creases. A carefully selected level of biaxial prestrain yields a closed 3D topology—a pyramid. Other 3D geometries that resemble a cylindrical shell and a windmill were also possible with a similar approach while creases with certain configuration need to be designed.\[220\] It is worth noting that experimental technique other than simple thickness control may also be used to produce creases. For
example, researchers used low-energy ions in reactive ion etching and high-energy ions in focused ion beam to achieve the control of strain at nanometer scale, and various origami assemblies of 3D structures were obtained.[224] Leong et al.[225] demonstrated the possibility of producing hinges composed of a metallic bilayer. For nanomembrane made from surface-decorated metal nanostructures, it was noticed that a “gentle” focused ion beam-milling can partially remove the binding ligands and induce local heating, which resulted in local stress buildup and folding of nanomembrane, and origami structures were obtained by programming the milling parameters.[78,80]

In many experimental works, the driving forces of self-assembly came from the compressive buckling effect during releasing the pretrained substrates. Several modified approaches have also been proposed to further expand the diversity of the obtained 3D structures. First, with carefully configured residual-stress layers, complex buckling modes can produce previously inaccessible 3D structures.[226] Second, elastomeric substrates with engineered distributions of thickness yield desired strain distributions, and thus complex 3D structures were obtained by compressive buckling.[227] It is worth noting that the driving force may not come from the substrate at all. Published papers showed the possibility to realize 3D origami structures by utilizing energies like magnetic field, polymer swelling, thermal actuation, ultrasonic pulse, etc.[228] The left panel of Figure 6d shows pictures of a patterned 2D precursor made from metal nanomembrane. The 2D precursor then self-assembled into a cube under the influence of the surface tension of the molten solder (right panel of Figure 6d).[229]

In the left panel of Figure 6e, a hockey-stick-shaped nanomembrane is patterned by reactive ion etching, and the internal strain therein makes it roll/bend into a helical structure (right panel of Figure 6e).[49]

The development of kirigami and origami assembly structures provides the possibility of producing unusual electromagnetic and optical devices which would be difficult or impossible to access through conventional approaches. For instance, Zhang et al.[102] provided a device demonstration in the form of a mechanically tunable optical transmission window, where a kirigami-inspired structure was used to block the light path by controlling the strain status. Optical applications of 3D origami were also reported by Cho et al.[230]

With the development of this 3D self-assembly technique, more devices with complex geometries and advantageous functions have been fabricated.[231] Figure 7a demonstrates a 3D spiral inductor for near-field communication as an example. The applied external strain can lead to obvious morphological evolution of the device (see simulation in panel (i) of Figure 7a). The measured inductance at a frequency of 13.56 MHz as a function of external strain is demonstrated in panel (ii) of Figure 7a and the values from simulation are also plotted for comparison. The inductance increases slightly with the strain, which was ascribed to the transformation of the morphology and corresponding change in energy losses.[232]

Geometrical evolution in response to stimulations from external field may lead to tunable or even smart devices. In such cases, the initial configuration is 3D but the response to external stimulation causes the programmed action of the materials/structures, which creates time dependence of the configuration and is looked as the fourth dimension. The structures are thus called as 4D structures. As an example, the dynamic control of the morphology of origami structure was realized by the addition of the polymer layer at the crease/hinge position, and the mechanical property of the polymer can be altered by heat or chemical reaction.[233] Figure 7b shows a microgripper structure prepared with the modified crease, and Cr/Cu bilayer was used as stressor. Before thermal or chemical actuation, polymer was stiff to prevent the flexing of the hinge, thereby keeping the gripper flat and open. When the mechanical properties of the polymer were altered, the Cr/Cu bilayer beneath was allowed to flex, resulting in the closure of the gripper >40 °C. Panels (i)–(iv) of Figure 7b demonstrate that it is possible to retrieve a dyed bead when the microgripper is triggered by heat.[234] Similar smart or remotely controlled device might be used to encapsulate microobjects like cells, and thus may have important applications in sensing and biology fields.[234–238] We expect that more responsive materials corresponding to various external stimulations can be incorporated with nanomembrane structures in the future and the applications of these advantageous 4D devices will be largely expanded.

The flexible 3D origami structures with electrical devices can be intimately integrated with organs or tissues in animal or even human bodies to achieve real-time mapping and manipulation of electrophysiology, and thus attracted increasing interest recently.[239,240] Figure 7c shows an optical microscopy image of the brain probe fabricated by using a self-assembly process.[241] The release of the internal strain makes the porous nanoelectronic network form a cylindrical probe structure. Local tensile strain elements in the supporting arms are incorporated to produce negative curvature, bending the devices away from the surface of the cylinder and thus each sensor element is about 100 µm away from the cylindrical probe surface (panel (i) of Figure 7c).[241] The high flexibility of probe allows positioning without moving the implanted portion within the tissue. Acute recording experiments made in the somatosensory cortex of an anaesthetized rat (panel (ii) of Figure 7c) demonstrate the capability for larger-scale multiplexed recording local field potentials with this probe.[241] These kind of structures thus can be used as neuron–nanoelectronics interfaces for many in vivo studies.

5. Biomimetic Nanomembranes

Every living cell, from bacteria to the cells in human bodies, has nanomembranes acting as interfaces between the cytoplasm and extracellular matrix. All metabolic processes proceed through nanomembranes and involve their active participation. Compared with the nanomembranes in biology, the man-made artificial nanomembranes have similar geometrical features but they lack complex functionalities. As a research field with rapid development, more complex functionalities may be incorporated into the artificial nanomembranes in the future. Currently, there are mainly two approaches used to fabricate nanomembranes with potential biofunctions. The first is to design nanomembranes with specific composition and structural properties, which have certain biofunctionalities. With the
deep understanding of the structural properties from the molecule scale and the continuous optimization of the composition, more biological activities have so far been realized[242,243]. Man-made nanomembranes of macroscopic size and nanometric thickness have already found advantageous applications in drug-delivery vehicles, biomimetic systems, microfluidic valves, platforms for biosensors, wound dressing, and even artificial organs.[244] Especially, many efforts have been made to create nanomembranes assembled from lipids, or synthetic analogues of lipids (e.g., lipid-like peptides, block copolymers).[245,246] Due to their unique properties, peptoids are recently considered as synthetic analogues of lipids.[247] Jin et al.[248] designed a series of amphiphilic, lipid-like peptides, and assembled peptoids into nanomembrane through an evaporation-induced crystallization process. The simulation demonstrated the formation of strips of hydrophilic domains along the x direction on nanomembrane surface (panel (i) of Figure 8a). A typical AFM image of this self-assembled peptoid nanomembrane is shown in panel (ii) of Figure 8a, and corresponding inset exhibits optical image of the sample. The fabricated nanomembrane is stable after heating to 60 °C in water overnight. The nanomembranes can also survive when
they were placed in ethanol for over 6 h, in phosphate buffered saline (PBS) buffer (pH 7.4), and in 1 M Tris-HCl buffer (pH 7.4). The thickness variations of the nanomembrane in response to changes of Na\textsuperscript{+} concentration were also observed, as this phenomenon was associated with lipid bilayer. Another remarkable property of this nanomembrane is its ability to self-repair. The assembled nanomembranes possess similar properties of biological lipid bilayer and are considered to provide a robust platform to incorporate a diverse range of functional objects as peptoid side chains. Similar self-assembled nanomembrane structures with biofunctions may have applications in electronics, water purification, surface coatings, biosensing, energy conversion, and biocatalysis.

The second approach is to use nanomembranes as substrates or scaffolds for cell culture, which provide platforms for detailed investigations concerning biobehaviors of the cells. In addition, nanomembranes were intensively investigated for possible applications in tissue engineering. Extracellular matrix in native tissues has an ideal structure and function to direct the cellular organization and therefore to regenerate the tissues and organs. In order to mimic this matrix, nanomembranes made from different materials and decorated with functional groups were characterized. These nanomembranes can serve as an excellent microenvironment for cell adhesion, migration, proliferation, and differentiation, and the mechanical properties of the cell layer can thus be measured directly. As a pioneer work, Kang et al. investigated an epithelia layer formed by a kidney cell line. The researchers seeded the MDCK cells on a nanomembrane (panel (i) of Figure 8b) and cultured the cells to confluence. The experimental results demonstrate the epithelia formed nice cell–cell junctions. Under 10\% and 20\% stretching conditions, the cell–cell tight junctions were preserved, while the 30\% and 40\% stretching conditions led to gradual degradation of the junctions. The junctions become obviously disrupted after subjection to 20 min of an 80\% stretched state, as shown in panel (ii) of Figure 8b. Detailed quantitative analyses indicated that the Young's modulus of the intact cell monolayer was \( \approx 20 \text{kPa} \). This work suggests that the biomimetic nanomembrane is capable of monitoring cell–scaffold interaction noninvasively and in near real-time.

The (self-)assembled 3D structures may also be used for biological applications. As typical self-assembled structure, the microtubes made from rolled-up nanomembranes, has been used for cell culture experiments. The mechanical interactions between the cells and the rolled-up nanomembranes were found to influence the arrangement of the inside cells (panel (i) of Figure 8c). Although the yeast cell was alive in the small microtube, the bioactivities of the cell were suppressed due to nutrition shortage.

![Figure 8](image-url)

**Figure 8.** a) Assembly of lipid-like peptoids into biomimetic nanomembrane. (i) Space-filling molecular model of the nanomembrane. (ii) AFM image of the self-assembled nanomembranes. The inset is the optical image of the gel-like material containing a large number of free-standing nanomembranes. Adapted under the terms of the Creative Commons Attribution 4.0 International License. Copyright 2016, Nature Publication Group. b) Mechanical properties of the cell layer are studied with the help of a flexible nanomembrane. (i) A schematic diagram of the MDCK cell monolayer on a nanomembrane. (ii) Staining image of the damaged cell junctions after 80\% stretching test for 20 min. Adapted with permission. Copyright 2013, WILEY-VCH. c) Guided cell growth by rolled-up nanomembrane. (i) Optical microscope images of four different microtubes containing yeast cells and the tube diameters are decreased from left to right. Reproduced with permission. Copyright 2008, Royal Society of Chemistry. (ii) SEM image of guided growth of neurites. Reproduced with permission. Copyright 2011, American Chemical Society. d) Rolled-up nanomembrane mimicking tubular structure in tissue. (i) Different cells distribute in 3D as the wall of the tube, in a fashion similar to blood vessels: endothelial cells, smooth muscle cells, and fibroblast cells from inside out. (ii) Magnified and side views of a portion of the tube in (i), indicated by the dashed line. Reproduced with permission. Copyright 2012, WILEY-VCH. e) 3D DNA origami. (i) Schematic representation of the nanoflask. (ii) AFM images of the nanoflask. Adapted with permission. Copyright 2011, American Association for the Advancement of Science.
microtubular geometry can even guide the growth direction of the axon (panel (ii) of Figure 8c).[259,260] and the cells growing inside the microtubes demonstrated increased photoresistance.[259] Recently, Schmidt and co-workers investigated the interactions between rolled-up microtube with different mammalian cells, and their influences on cellular events were investigated in detail.[261–263] It is expected that these 3D structures can be used to gain molecular insights into key cellular events occurring in 3D microenvironments.

Obviously, the tubular geometry is considered as in vitro mimic of a blood vessel.264 In fact, tissues with tubular structures are abundant in the bodies of higher animals.265 In addition to the 3D structures, tubular tissues in the bodies have different types of cells at specific locations (i.e., different parts of the tube wall are made up of different cells).266 Researchers thus tried to produce rolled-up nanomembrane with layered walls made of multiple types of orientated cells.265,267 The strategy is to deliver and pattern different types of cells on a nanomembrane using microfluidic channels before rolling process.265,267 Panel (i) of Figure 8d shows such a rolled-up tube, and the enlarged image is shown in panel (ii) of Figure 8d. This structure is similar to the human vessel: the wall has three layers, and in each layer there are one type of cells: endothelial cells (red), smooth muscle cells (green), and fibroblasts (blue) from inside to outside. Cell culture experiment proved that most cells are alive inside the tube wall.265 Moreover, the orientation of the cells (circumferentially or longitudinally aligned) can be controlled inside the tubes by topographical contact guidance.255,265 It is believed that this approach of producing mimics has potential to recapitulate functional tubular structures for tissue engineering.266 The recent progress in preparing rolled-up tubular structure made from biodegradable materials further paves the way for practical applications to patients.268

We should mention that there are a new kind of 3D nanomembrane structures made from DNA, which is called DNA origami.269–271 In such structure, a long single strand of DNA is folded into arbitrary shapes by hybridizing with hundreds of short DNA strands.269 The structure can be further functionalized with various biomolecules and nanoparticles.272,273 The “nanoflask” DNA origami shown in Figure 8e reflects the level of complexity that can be produced by this technology.274 Here, out-of-plane curvature is introduced by adjusting the particular position and pattern of crossovers between adjacent DNA double helices.274 The neck of the flask has a constant diameter of 13.2 nm, whereas the round bottom is composed of several different ring sizes (panel (i) of Figure 8e). Panel (ii) of Figure 8e shows corresponding AFM images of the fabricated nanoflasks. Recent attempt also demonstrated the possibility of developing nanomachines from DNA origami by creating dynamic mechanisms.275 DNA origami is believed to have great potential in clinical use such as antitumor drug delivery platforms.271

As the last part of this section, we should mention that the biomimetic nanomembranes in fact have a broad spectrum of applications in the fields other than biology. For instance, biomimetic moth eye nanostructure was fabricated on the surface of the nanomembrane by soft nanoimprint lithography. The structure allowed the efficient light trapping over the entire solar spectrum, and a 22.2% enhancement of light harvesting in fabricated solar cells was achieved.276 The usage of biomimetic nanomembranes in proton-exchange membrane for fuel cell application was also explored.277 More biomimetic nanomembrane structures possessing interesting properties are currently being investigated and their application potentials will attract increasing attentions.

6. 2D Materials in a Nanomembrane Format

2D materials made from naturally layered materials (van der Waals solids) are atomically thin,23,31,32 and therefore can be considered as the thinnest margin of the nanomembrane structures. The stack of multilayers with larger thickness thus well fits the definition of nanomembrane.278 Since the fabrication of graphene in 2004,23 the 2D materials related researches have become one of the hottest topics. So far, more than 140 2D materials besides graphene are known.83,279 As discussed in Section 1, these 2D materials as nanomembranes are mainly extracted from layered bulk materials or grown artificially by several methods like vapor phase deposition and wet chemistry synthesis. Some scientists also used a two-step process which included first depositing metal then sulfurizing the metal layer to prepare transition-metal dichalcogenide nanomembranes.280 The 2D material nanomembranes present physical properties that are unique because of the low dimensionality and their special microstructures. Various properties of 2D material nanomembranes such as their mechanical, electrical, optical, and thermal properties were studied to provide an accurate perspective.281 Investigations demonstrate that although the unique properties are closely related to the 2D geometry, they are still strongly material-dependent. For instance, Wang et al.277 studied the mechanical property of free-standing zinc hydroxy dodecyl sulfate (ZHDS) hexagonal nanomembrane by nanoindentation. Compared with ZnO nanomembrane, the layered ZHDS nanomembrane demonstrated much different behavior: unloading-loading test showed the ZHDS nanomembrane had viscoelasticity. In addition, the ZHDS nanomembrane was much soft with a 0.2 GPa hardness while the ZnO nanomembrane possessed a 3.2 GPa hardness. Sledzinska et al.282 investigated the thermal property of MoS2 polycrystalline nanomembrane both experimentally and theoretically and revealed a 100-fold reduction in thermal conductivity with respect to the bulk. The strong reduction was related to scattering on grain boundaries, and therefore it is possible of tailoring thermal conductivity by controlling the grain size in the nanomembrane.282 Mortazavi et al.283 investigated the mechanical property of Mo2C nanomembrane by simulating uniaxial tensile stress along the armchair and zigzag directions. The results indicated that the elastic properties were close along various loading directions. In addition, the Mo2C nanomembrane presented negative Poisson’s ratio and thus can be categorized as an auxetic material.283 The corresponding optical spectra of relaxed and stretched nanomembranes with the electric field parallel to the plane were changed significantly, while the optical spectra with the electric field perpendicular to plane were not changed.283

Due to these interesting properties, devices such as transistors, memories, photodetectors, and photocatalyzed hydrogen...
evolution reactors based on multilayered 2D material nanomembranes have been reported, and the number of related publications is increasing rapidly. In particular, free-standing nanomembranes with a thickness of a few nanometers were predicted to possess a superior performance in the separation of materials, because they can allow a faster passage of the selected ions or molecules. As a step further, the ion transport characteristics in the graphene nanomembrane were investigated in detail. A similar approach was also used to measure DNA translocation by using graphene nanomembrane with electron-beam fabricated nanopores. Due to their long mean-free path, high Fermi velocity, and excellent charge dissociation ability, the 2D material nanomembranes found advantageous applications in photovoltaic devices. The fabrication processes are compatible with Si planar process and solar cells with high efficiencies can be obtained. Moreover, the large specific surface area and the in-built selectivity due to their varying affinity for different analytes made some 2D material nanomembranes suitable for high sensitive gas sensing applications. Panel (i) of Figure 9a shows a photograph of a gas sensor made from MoS$_2$ nanomembrane. Experimental results indicate the sensor sensitivity is linearly proportional to the concentration of NH$_3$ introduced (panel (ii) of Figure 9a), which makes determination of gas concentration feasible. 

Another way to produce 2D material nanomembranes is to fabricate composite nanomembrane consisting 2D materials. Composite nanomembranes made from 2D materials and carbon nanotube have been reported, and various applications have so far been demonstrated. It was later reported that a composite structure can be obtained by intercalating polymer between the layers of the 2D materials. Panel (i) of Figure 9b shows a schematic diagram of the Ti$_3$C$_2$T$_x$–sodium alginate (SA) composite, which demonstrates a layered structure. The composite nanomembranes have additional advantages such as high conductivity, easy processing, relatively low density, and mechanical flexibility, and their electromagnetic interference (EMI) shielding abilities were explored. With increasing Ti$_3$C$_2$T$_x$ content, EMI shielding effectiveness (SE) increases, to a maximum of 57 dB for the 90 wt% Ti$_3$C$_2$T$_x$–SA composite nanomembrane, as shown in panel (ii) of Figure 9b. The use of composite nanomembrane in this case attained excellent performance and meanwhile remarkably reduced the weight and material consumption.

In line with continuous advances for the synthesis of 2D materials and their (self-)assembled structures, new fabrication technologies with convenience and low cost and potential applications of these materials/structures have been intensively explored. Similar to aforementioned origami/kirigami structures, researchers also fabricated 3D structures from 2D materials. As shown in panel (i) of Figure 9c, the graphene kirigami can undergo large strain and pulling the kirigami structure caused the graphene strads to pop out and deform out of plane. Mu et al. prepared graphene-based bilayered paper where one layer consisted graphene–polymer composite. This layer can swell/shrink in response to environmental humidity, temperature, or NIR light, leading to bending/ unbending of the nanomembrane.
flat geometry. There are other driving forces that have been engaged to produce bending/rolling or 2D materials. For instance, electric field interaction between 2D material and liquid, friction force, surface hydrogenation, magnetic field, and nanoparticle aggregation have demonstrated their ability in producing 3D (self-)assembled structure from 2D materials. As a typical example, a TEM image in panel (iii) of Figure 9c shows a rolled-up graphene layer. The tube-like structure with a hollow core surrounded by wall consisting of graphene layers can be clearly observed.

7. Conclusion and Outlook

The nanomembrane is defined as structures with thickness limited to about one to several hundred nanometers and with much large lateral dimensions. This kind of structures bridge the gap between nano and macroscales, and various interesting properties and amazing applications associated with unique geometry can be expected. So far, many advanced materials have been studied in the format of nanomembranes. The spectrum of nanomembrane materials spans a wide variety of inorganic and organic materials, including biomimetic and 2D materials, and many technical approaches have been developed to produce corresponding nanomembrane structures. The nanomembranes, possessing quasi-2D geometry, have large lateral dimension with flexible feature, and can be (self-)assembled into 3D shapes in deterministic manners with curvilinear surfaces. In such cases, the combination of the excellent properties of the constitutive materials (or hybrid multilayer) with the 3D geometries produces addition values to the nanomembrane field. The unique features from the materials and the structures make nanomembranes highly attractive for flexible electronics, nanophotonics, robotics, etc. In this review, we summarized recent progresses in the research field of nanomembranes, where the (self-)assembly processes in fabricating 3D structures have been emphasized. A huge number of diverse structures and functionalities have been realized with a broad range of materials and material combinations. Interesting applications in many areas are intensively explored and more potentials should emerge in the future.

Due to the present accelerating progress in this field, rapid advances may well be expected in the near future. The available materials, structures, and processes can be far extended both into the inorganic and the organic worlds. Besides those universal technologies summarized in this review, we hope more case-dependence fabrication technologies can be developed to realize precise and controllable fabrication of nanomembranes from certain materials. Manipulating the mechanical properties and the stress/strain within the nanomembrane spatially and controllably will be utilized to shape the nanomembrane into 3D geometries deterministically. Since an exceptionally large number of 3D structures have been and will be fabricated by (self-)assembly processes, we hope practical devices can be obtained based on these 3D structures, and their dimensions may be expanded ranging from nanoscale to macroscale for corresponding applications. The technology compatible with Si planar process may help to produce integrative systems with multifunctions. Most importantly, more materials which can behave in response to external stimulations may be incorporated into the nanomembranes and structures known as 4D structures can be fabricated. Micro/nanoactuators or micro/nanorobots based on nanomembranes have already been fabricated by using this idea, but much future work is still needed to realize overall optimization of the structures that can respond to different stimulations with large forces and high sensitivity, selectivity, and speed. In addition, 2D material nanomembranes have attracted increasing interest. Composite nanomembranes fabricated by stacking 2D nanomaterials and layers of other materials (by, e.g., transfer printing) may represent another important direction of the nanomembrane field. The intriguing (self-)assembled 3D structures made from these composite nanomembranes may have additional new physical and chemical properties which could lead to novel device concepts. Overall, future investigations in this field should be focused on the nanomembranes and their 3D assemblies, in the aspects of both fundamental science and advantageous applications. We expect that these structures should have great potentials in electronics, optical devices, energy harvesting devices, single cell analysis systems, cells/tissue engineering, lab on a chip, micro-/nano-electromechanical systems, and many others.

Acknowledgements

The authors would like to thank Prof. O. G. Schmidt, Prof. J. A. Rogers, and M. G. Lagally for fruitful discussions. This work was financially supported by the Natural Science Foundation of China (Grant Nos. 51711540298, 61628401, U1632115, and 51475093), Science and Technology Commission of Shanghai Municipality (Grant No. 17C1401700), the National Key Technologies R&D Program of China (Grant No. 2015ZX02102-003), and the Changjiang Young Scholars Program of China.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

3D structures, assembly, nanomembranes, origami, self-assembly

Received: October 20, 2017
Revised: November 19, 2017
Published online: January 2, 2018


