Two-Dimensional Nanomembranes: Can They Outperform Lower Dimensional Nanocrystals?

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Since the discovery of nanoparticles and quantum dots (QDs), surfactants have often been their companions because of their indispensable roles in stability, shape, and size control. Shape transformation from 0D to 1D nanocrystals (*i.e.*, quantum rods and nanorods) has been achieved using surfactant molecules such as hexyl-phosphonic acid, hexadecyltrimethyl ammonium bromide, or oleic acid in the growth of CdSe,[1] Au,[2] or TiO_2 nanorods.[3] Surfactants such as linear amines have also been used to increase the dimensionality of cobalt nanoparticles to two-dimensional (2D) structures[4] and to form zirconium disulfide nanodisks;[5] similar molecules such as stearic acid, arachidic acid, or octadecyl amine have also been used for directing 2D growth in iron nanostructures.[6] In general, the presence of surface adsorbed surfactants modulates the growth rate of different nanocrystal facets and promotes an anisotropic crystal growth.[7,8]

One fascinating aspect of 0D and 1D nanoparticles has been the manifestation of size-dependent properties and quantum effects; however, so far, realization and utilization of such effects in technological applications have yielded results far below expectations. One key reason is likely the difficulty in accessing individual particles due to their small size using current fabrication techniques. Discovery of the self-assembly of nanoparticles into 2D networks[9,10] shaped one of the premises of nanotechnology, namely, bottom-up syntheses of materials by design, and offered the use of the collective properties of nanocrystals in their ensemble. The latter was perhaps also an evolutionary remedy to make commercial integration of nanocrystals more facile using conventional

ABSTRACT Inorganic nanomembranes, analogues to graphene, are expected to impact a wide range of device concepts including thin-film or flexible platforms. Size-dependent properties and high surface area—two key characteristics of zero- (0D) and one-dimensional (1D) nanocrystals—are still present in most nanomembranes, rendering their use more probable in practical applications. These advantages make nanomembranes strong contenders for outpacing 0D and 1D nanocrystals, which are often difficult to integrate into commercial device technologies. This Perspective highlights important progress made by Wang *et al.* (doi: 10.1021/nn2050906) in large-scale fabrication of free-standing nanomembranes by using a solution-based technique, as reported in this issue of *ACS Nano*. The simplicity of this new approach and the elimination of typical delamination processes used in top-down nanomembrane fabrications are among the strengths of this technique. Areas for improvement along with an overview of other related work are also discussed.
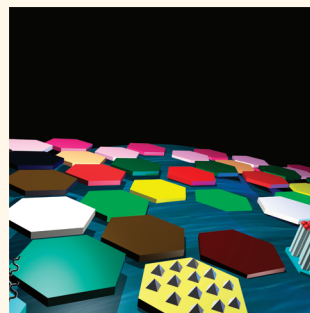
approaches, which, indeed, remains something to be seen. However, because these assembly processes are self-driven, their hierarchical order and size have been shown to be difficult to control and often limited in scale. As a result of the challenges in the controlled assembly of 0D nanocrystals, directed assembly with an intense focus on nanorods and nanowires brought new advances to large-scale manipulation and integration of nanowire-based devices, for example, in thin-film electronics,[11,12] electro-optical devices such as sensors,[13] light-emitting diodes,[14] and high mobility transistors.[15] It is interesting to note that the key innovation in all of these platforms has been the use of 2D assemblies of nanowires—a distinct characteristic that can also be achieved using inorganic nanomembranes, which have been a less known member of this family until recently.

Researchers have known of inorganic nanomembranes for at least two decades,[16,17]

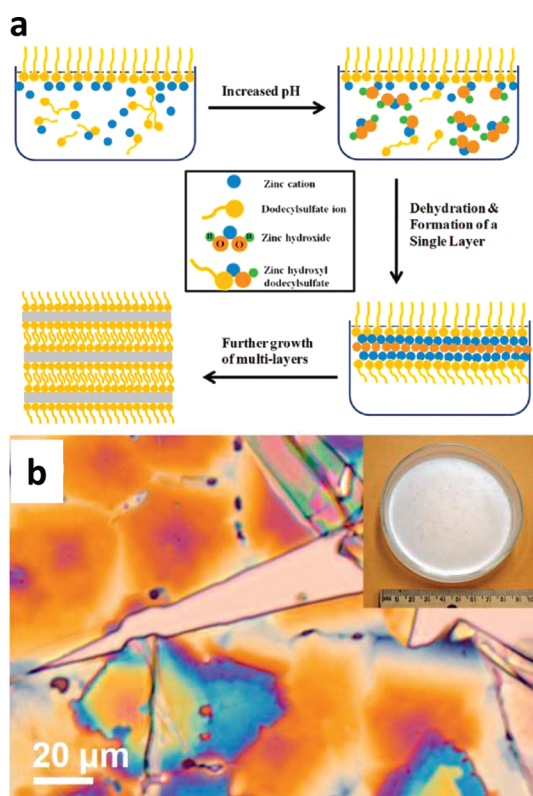* Address correspondence to babak.nikoobakht@nist.gov.

Figure 1. (a) Large-scale formation of zinc hydroxydodecylsulfate thin membrane at the water−air interface and the role of sodium dodecylsulfate are schematically illustrated. (b) An optical microscope image of part of a zinc hydroxydodecylsulfate nanomembrane. The inset image represents the top view of the as-synthesized nanomembrane on the water surface in a glass dish. Reprinted from ref 30. Copyright 2012 American Chemical Society.

but these nanomembranes have recently recaptured significant attention. From a basic science viewpoint, this increased attention is due to the rich science of nanomembranes, with size-dependent properties including optical properties,[18] thermal conductivity, and electrical conductivity. From a device-integration perspective, nanomembranes are well suited for incorporation into other materials and offer the unique opportunity of utilizing their size-dependent properties in commercially viable products, something that has not been realized for lower dimension nanocrystals. Nanomembranes become even more attractive because the existing knowledge on 0D and 1D nanoparticles, such as composition control, doping, heterostructure growth, and nanomanipulation, can be extended to nanomembranes as well.

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Two-dimensional structures with nanoscale thickness have been commonly used in the epitaxial crystal growth world and played an essential role in semiconductor lasers, and photodetectors.[19] More recently, such layered structures have been transferred to a variety of substrates using top-down approaches.[20−22] To release a thin slab of epitaxial 2D structures from a mechanical support, it is necessary to place a sacrificial layer between the substrate and the to-be-released membrane. In epitaxially grown layers, there needs to be a match between the sacrificial layer and the overlayer, which has been readily accomplished in many materials systems (*e.g.*, lattice-matched AlAs or InGaP as the sacrificial layer for GaAs- and InGaAs-based systems and lattice-matched InGaAs as the sacrificial layer for InP-based systems). One advantage here is that superlattices composed of alternating layers of heterogeneous materials with multiple embedded sacrificial layers can be used during the epitaxial growth process, thus enabling the release of multiple stacks of membrane either simultaneously or sequentially. Membranes formed by epitaxial methods can also be engineered with specific optical and electronic properties, such as the use of potential barriers for electron or light confinement, which are suitable for photovoltaic applications.[23] Another advantage is that the released membranes—semiconductor, dielectric, or metal—can also bend, twist, and roll to form three-dimensional (3D) membranes, depending on the embedded strain and aspect ratio of the membrane.[22,24−27] Although this is a dexterous methodology, potential limitations may include the need for single-crystal substrates for the formation of crystalline membranes, or extra steps may be necessary in the formation and release of stacks of membranes, which could add to the overall cost.

Bottom-up chemical techniques have also been used for the growth of large-area nanomembranes. One of the advantages of such methods
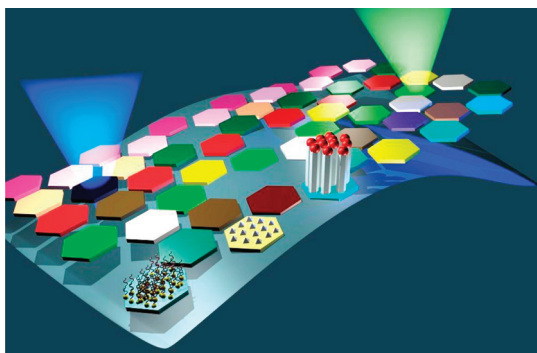
Figure 2. Nanomembranes or 2D nanostructures are of great interest in both basic and applied sciences. This illustration depicts nanomembranes as versatile vehicles for integration to flexible or soft surfaces with a wide range of applications, and substrates for epitaxial growth of lower dimensional nanocrystals.

is the potential for creating diverse nanostructures that either cannot be made by other techniques or are difficult to make. The rich science developed around lower dimension nanocrystals can be linked and used for creating 2D structures as well. In this regard, it has been shown that 2D networks of PbS QDs with cubic structures can be converted to 2-nm-thick nanosheets with lateral dimensions of a few hundred nanometers; in this collective shape transformation, more active facets (110) of neighboring QDs disappear in a process driven by the use of a surfactant (oleic acid) as the template and surface energy is minimized among the QDs.[28] Wet chemical techniques can also be used to break down less-ordered materials into more-ordered structures by meddling with molecular forces such as van der Waals interactions. Solvent exfoliation, as an example, has been used to produce single- or multilayer crystalline sheets of some transition metal oxides or dichalcogenides such as MoS_2, WS_2, $MoTe_2$, and Be_2Te_3.[29] These materials, like graphite, are naturally layered structures; by using this technique and appropriate solvents, these materials can be dispersed as thin sheets and eventually as thin-film composites with modified electronic, thermal, or mechanical properties.

Diversifying growth methods and controlling the single-crystalline structure of formed nanomembranes are

among the existing challenges. In this issue of *ACS Nano*, Wang *et al.* extend the growth of nanomembranes using surfactant-directed surface assembly at the water–air interface and produce wafer-scale-thin layers of zinc hydroxy dodecylsulfate.[30] The formed nanosheets can be transferred to a variety of substrates and surfaces and converted to ZnO 2D membranes by processes such as thermal annealing. In their approach, negatively charged dodecylsulfate ligands are used in a concentration regime where surfactants can form close-packed assemblies at the water–air interface with the hydrophobic side of the ligands facing the air (Figure 1a). The polar head groups of the surfactants host the Zn cations in a sandwich format. In surfactant-assisted nanocrystal growth, cations and anions undergo a rapid reaction to form nanocrystals that instantaneously bind to the surrounding surfactants to reduce their surface energy. If surfactant ligands form a certain template in solution then the nanocrystal growth could be guided; however, often the template morphology is disturbed by the presence of cations and anions. The main cause is a change in the head-group size of surfactant ligands and, thus, a change in the electrostatic forces among the head groups, leading to variations in the overall size and shape of the surfactant assemblies. Therefore, growth strategies must be developed to mitigate the negative impact on the surfactant

head groups. Taking this into consideration, Wang *et al.*[30] increase the pH of the growth solution by thermal decomposition of hexamethylenetetramine, which also acts as the buffer agent. The release of ammonia as a decomposition product gradually increases the concentration of hydroxyl groups, causing crystallization of zinc hydroxyl species on the dodecylsulfate polar surface; it also allows for a controlled precipitation reaction, avoiding rapid release of ZnO from solution. A similar strategy has been used in the growth of monodisperse CdS QDs where thiourea was used to release sulfide ions homogeneously and slowly in aqueous cadmium solutions.[31]

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In the manipulation of nanomembranes for device applications, it is important to control the number of stacked layers on a given surface. Top-down approaches enable great control over this parameter but solution-based techniques do not offer such mechanisms. This is evident, for instance, in the solvent-exfoliation technique[29] in which dispersed layered materials form multilayers once deposited on a surface. This stacking tendency is typically due to the attraction forces between the single sheets. The approach reported by Wang *et al.*[30] may offer a new opportunity, as a supersize single layer of zinc hydroxydodecylsulfate forms at the air–solution interface and can be

transferred to a solid surface (Figure 1b). Wang *et al.*[30] also examined some of the electrical properties of such 2D structures in wet and dried states by fabricating field-effect transistors. They noted lower electron mobilities compared to typical ZnO films. This was attributed to the existence of water in the structure which should improve through further dehydration. The results of this report can reinvigorate the use of surfactants in solution growth of a variety of novel semiconductors and large-scale metal nanosheets.

Outlook and Future Challenges. Synthesis and fabrication of nanomembranes is expected to grow and encompass a diverse range of technologically important materials such as II−VI, III−V, and IV semiconductors. As schematically shown in Figure 2, considering their thin geometries and advances in micro- and nanofabrication techniques, a whole host of designs and material combinations are envisaged for realization of smarter materials, for example, in thin-film photovoltaics, light energy storage, and thermo-electricity. To explore the potentials of this class of nanocrystals fully, new synthetic routes are needed, for instance, for their heterojunctions, bandgap engineering, full doping, and partial doping. In device integration, understanding the contribution of surface states and the effects of membrane shape or structural strain on light, charge transport, or energy transport is key for optimizing the mobility or charge-separation efficiencies.[32] Maintaining pristine surfaces of the membranes is critically important for many types of devices including MOSFETs, lasers, and solar cells, in order to avoid surface recombination or scattering of carriers. In the case of solution-based approaches, the state of the surface and the contributions of surfactants or their residues on electro-optical properties of the membranes need to be understood. Other challenges related to controlling nanomembranes' morphology

and assembly include controlling the homogeneity in their dimensions and developing methods for their transfer and positioning on surfaces.[33] Among the less-explored areas is the formation of heterojunctions or interfaces on nanomembranes with other materials including molecules, solid surfaces, QDs, or nanowires, which are considered gateways to important areas such as sensing, electronics, and tissue engineering. Nanomembranes have been shown to preserve most of their properties in out-of-plane modes,[34] which has also made them excellent candidates for implementation in 3D architectures in ordinary products such as clothing, automobile coatings, and glasses. They can also be integrated in more advanced products such as airplanes and unmanned vehicles, with applications in thin-film batteries, cooling devices, micropower generators, powerful sensors, and analyzers. Regardless of the dimensionality of nanocrystals, it is clear that harnessing their exciting and unique properties will continue to drive innovation. In searching for new materials with better properties and performance, the question to pose is, what new technology horizon can be reached with combination of our imagination and materials at the nanoscale?

Conflict of Interest: The authors declare no competing financial interest.

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