DOI: 10.1002/masy.200851002

Supramolecular Assembly and Hybridization in Giant Nanomembranes

Toyoki Kunitake[1,2]

We demonstrated recently that large nanomembranes became available from inorganic, organic/inorganic and totally organic precursors. Spin coating of mixtures of acrylate monomers and zirconium butoxide (or tetraethoxysilane), when combined with simultaneous radical polymerization and sol-gel reaction, gave 10–30 nm thick, free-standing nanomembranes composed of metal oxides and crosslinked acrylates as interpenetrating network. This approach was extended to thermosetting resins (epoxy, melamine and phthalic resins), to fabricate robust, free-standing nanomembranes. Mechanical properties of the nanomembranes as measured by the bulge test and by a compression method were comparable to those of the corresponding macroscopic resins.

The hybrid nanomembrane was subsequently prepared by supramolecular assembly of the nanofilm with surfactants and lipids. These amphiphiles produced adsorbed monolayers on the nanomembrane and some of the assemblies were stably kept in water.

Keywords: hybridization; nanomembranes; supramolecular assembly

Introduction

The combination of nanometer thickness and macroscopic size facilitates important applications in materials separation, selective transport and electrochemical devices. Polymeric materials and inorganic materials have been used most frequently to fabricate practical separation membranes, but their thicknesses as independent entity basically remained in the micrometer range. Development of nanometer-thick, free-standing membranes is being accelerated in the last decade.

We define here "large nanomembrane" as having the following three features. First, its thickness is in the range of 1-100 nm. The self-supporting (free-standing) property is the second feature that is required for a membrane to be able to physically separate two spaces. Thirdly, the "large" nanomembrane should be characterized by an aspect ratio of size and thickness greater than 10^6; that is, if the membrane thickness is 10 nm, its size must be greater than 1 cm × 1 cm.

Nanomembrane Formation by Layer-by-layer Assembly

Novel approaches is being developed for molecularly thin layers. Most important is the electrostatic layer-by-layer assembly.[1] This method is now widely used for the lamination of oppositely charged polymers, polymers with proteins, and organic with inorganic compounds in the molecular thickness. Preparation of the layer-by-layer assembled ultrathin hollow polymer shells (or nanotubes) was extensively investigated by Caruso et al.[2] and by other groups.[3] The preparation of free-standing ultrathin films by this approach has been studied by several groups. Onda et al. prepared enzyme-containing alternate films on porous filter membranes and examined sequential enzyme catalysis.[4] Huck et al. isolated a free-standing hexagonal sheet (10-μm size and 5-nm thick) of alternate polyions.[5]

---

[1] The University of Kitakyusyu, 1-1 Hibikino, Wakamatsu-ku, Kitakyushu Japan
E-mail: kunitake@ruby.ocn.ne.jp
[2] Frontier Research System, RIKEN

Mamedov and Kotov prepared free-standing ultrathin films that incorporated magnetite nanoparticles by dissolving away a cellulose acetate support on glass substrate.[6] Tsukuruk and co-workers discussed the mechanical property of free-standing nanomembrane composites. Very recently, Ono and Decher obtained a free-standing polyelectrolyte multilayer with a few centimeter square size by using a suitable sacrificial layer.[8] The thickness of this film is estimated roughly as 250 nm from the reported number of the deposition cycle. Unfortunately, these LbL methods could give nanofilms (thickness 30–70 nm) with few tens to few hundreds of nanometers, as summarized by Jiang and Tsukruk.[7] More currently, Ma et al. material prepared a free-standing nanofilm (Thickness, 100–500 nm) from cross- linked PAA/PAH multilayer.[9]

Giant Nanomembranes of Metal Oxides

It is clear from the above examples that it is not easy to impart to a single membrane both of macroscopic size and nanometer thickness.

We have been studying a novel fabrication procedure of metal-oxide nanolayers by sequential sol-gel process.[10,11] A similar procedure was independently reported by Kleinfeld and Ferguson.[12] We attempted to apply this approach to the preparation of self-supporting metal oxide nanofilms.[13] For example, a composite (polymer/metal oxide) thin layer was prepared on a sacrificial polymer underlayer, and then detached from the substrate by dissolving the polymer layer alone. Unfortunately, the size of the obtained ultrathin (polymer/metal oxide) composite film with thickness of ca. 20 nm could not be made larger than approximately 15 mm^2. The original film was fragmented readily upon dispersion in solvents.

These problems were solved by a new approach that included the use of designed "double layer" and spin-coating technique.[14] Photoresist polymers are suitable as sacrificial underlayer, since some of them are highly soluble in ethanol, and can be uniformly spin-coated onto a silicon wafer. On the other hand, PVA layer provides a homogeneous surface rich in the hydroxyl group, and it promotes the hydrolysis of metal alkoxide to form metal oxide layer homogeneously. Thus, a titania layer was formed from titanium butoxide by spin-coating on a double underlayer of PVA upper layer and photoresist lower layer on Si wafer. This specimen was placed in a Petri dish, and ethanol was added to remove the photoresist layer, leaving behind a free-standing ultrathin PVA/titania film. It is transparent, uniform and flexible. The corresponding SEM observation indicates that the membrane (3×4 cm) on an anodized aluminum oxide (AAO) disk is uniform and defect-free with 140 nm thickness (Figure 1). Much thinner membranes are available when dilute precursor solutions are employed, and a free-standing membrane with thickness of 13 nm was obtainable. As far as we know, this is the thinnest self-supporting membrane that can maintain its size as large as 10 cm^2 at least for several months. The major advantage of this approach over the previous surface sol-gel method is probably 2-fold. First, spin coating appears to give a more uniform layer over a large area than the chemical adsorption in the former, though monolayer adsorption is not assured. The second is the use of "double layer", in which the photoresist (TDUR-P015, Tokyo Ohka) layer facilitates membrane detachment and the PVA layer promotes 2-dimensional networking of nascent titania layer.

Subsequently, the spin-coating approach was extended to other metal oxide membranes.[15] Spin coating of various metal oxide precursors was performed on the double underlayer-coated Si wafer. Film thickness determined by SEM observation is strongly dependent on the kind of metal alkoxides, due to their different reactivity. The macroscopic and SEM pictures of a PVA/Al_2O_3 film are very similar to those of the PVA/titania film.

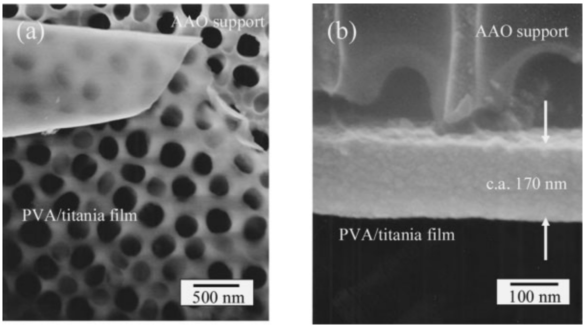

Figure 1.
SEM images of a PVA/titania film on an anodized aluminum oxide (AAO) support; (a) top view, and (b) cross-section view.

Nanomembrane of Organic and Inorganic Hybrids[16,17]

The spin coating process is effective for the preparation of macroscopically uniform, self-supporting metal oxide gel films with thickness of several tens of nanometers and lateral dimensions of several centimeters. Organic and inorganic hybrid materials with interpenetrating network structures combine advantages of organic polymers (versatility, flexibility and light weight) and the physical property of inorganic glasses (heat and mechanical resistance). This unique combination is effective for providing robust, free-standing nanomembranes. The fabrication procedure is rather simple. In the first example, the inorganic precursor was zirconium tetrabutoxide and the organic precursor was a combination of mono-functional monomer (4-hydroxybutyl acrylate), bifunctional crosslinking agent (hexanediol diacrylate), and photo-initiator (Darocure 4265). Simultaneous polymerization and polycondensation during the spin-coating process gives rise to nanomembranes of interpenetrated network of the two components, as schematically shown in Figure 2. A top-view SEM image of the resulting nanomembrane on an AAO support (Figure 3a and 3b) demonstrates formation of uniform 35-nm thick layer without defects and cracks. According to TEM observation (Figure 3c), a smooth, amorphous surface is formed for a specimen with the lowest zirconium dioxide (ZrO_2) fraction, but regular lattices with domain sizes of 5 to 10 nm is formed, when the ZrO_2 content is increased (Figure 3d).

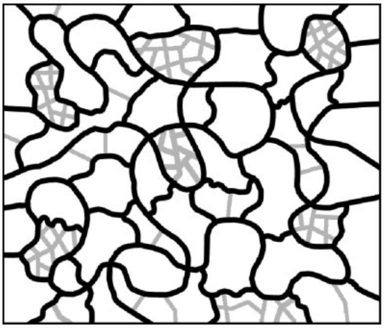

Figure 2.
Schematic illustration of the interpenetrated network of organic (in black) and inorganic (in yellow) components.

Totally Organic Nanomembranes

Fabrication of robust free-standing membrane is not limited to ceramic components and organic/inorganic hybrids. In general, hard materials, even if highly cross-linked, become soft when their sizes, thickness in particular, are reduced to the nanometer regime. Thermosetting resins are a representative class of the hard material, being insoluble and infusible upon cross-linking by thermal treatment. Epoxy resin is one of the favorable choices, since this resin is known to have superior properties in adhesiveness, dimensional stability, chemical

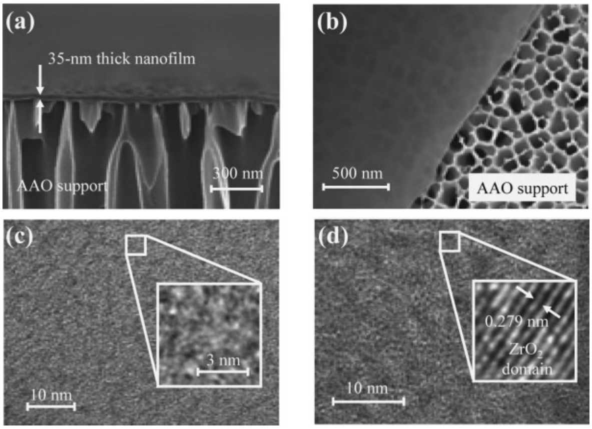

Figure 3.
Microscopic characterization of free-standing hybrid nanofilms. (a) SEM side-view image of a nanomembrane on AAO support. (b) SEM top-view image of a nanomembrane. (c) TEM image of a low-ZrO_2 nanomembrane on a copper grid. (d) TEM image of a high-ZrO_2 nanomembrane showing the presence of an ordered domain dispersed in an amorphous matrix.

resistance and electrical inertness. We have fabricated epoxy nanomembrane by spin-coating procedure using PHS as sacrificial layer.[19] The detached film maintained the size of the spin-coated area. A large, flexible film with a size of over 5 cm^2 was obtained even when the film thickness was as small as 20 nm (Figure 5a). The cross sectional view of the nanomembrane after transfer onto AAO support is given in Figure 5b. A uniform thickness of 23 ± 2 nm was obtained as the thinnest, free-standing nanomembrane without any signs of cracks and other defects on the membrane surface.

It is important to examine if the outstanding properties of the organic resin are retained even at the nanometer thickness. The tensile strength (σ) of the thinnest epoxy membrane was determined as 30 MPa, and this tensile strength is located within the range of 1–100 MPa that are found for the conventional thick epoxy resins of different compositions. The electrical property was studied by measurement of output leakage current using a potentiostat/galvanostat system. The nanomembrane was transferred on the surface of *p*-type silicon wafer, and platinum electrodes (1 mmφ) were evaporated on the top through the shadow mask to form the metal-insulator-semiconductor (*MIS*) stack, Pt/nanomembrane/*p*-Si. The output leakage current of the epoxy membrane (30 nm thick) was about 90 μA at 0.5 V and the electric

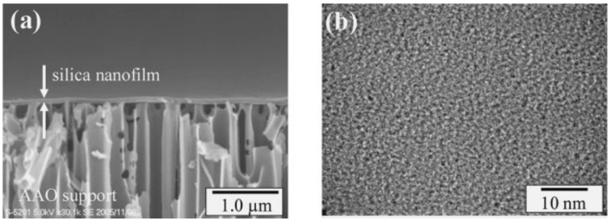

Figure 4.
(a) SEM side-view image of a SiO_2/polymer hybrid nanomembrane on AAO support. (b) TEM image of a SiO_2/polymer hybrid nanomembrane on a copper grid.

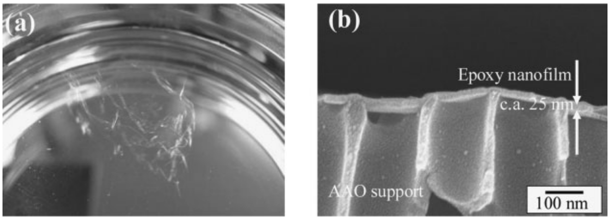

Figure 5.
(a) A epoxy nanomembrane in ethanol, and (b) SEM image of epoxy nanomembrane on AAO support.

resistivity was calculated as 0.5×10^{11} [Ω·cm]. The high electric insulation is another evidence of the defect-free feature of the nanomembrane. The conventional bisphenol A type epoxy resin gives a similar range of electric resistivity of 10^{10}-10^{12} [Ω·cm], and therefore, the electrical property remains essentially the same in the form of nanomembrane.

Similar organic nanomembranes are obtainable from other cross-linked organic macromolecules such as melamine resin, urethane resin and phthalic resin.[19] Typical chemical structures of these resins are shown in Figure 6. The physical property of these nanomembranes appears to reflect those of the corresponding macroscopic resins. For example, the urethane nanomembrane showed plastic deformation unlike other nanomembranes, when air pressure was applied in the bulge test. Successful fabrication of nanomembranes from rich combinations of precursor materials has an important bearing on functionalization

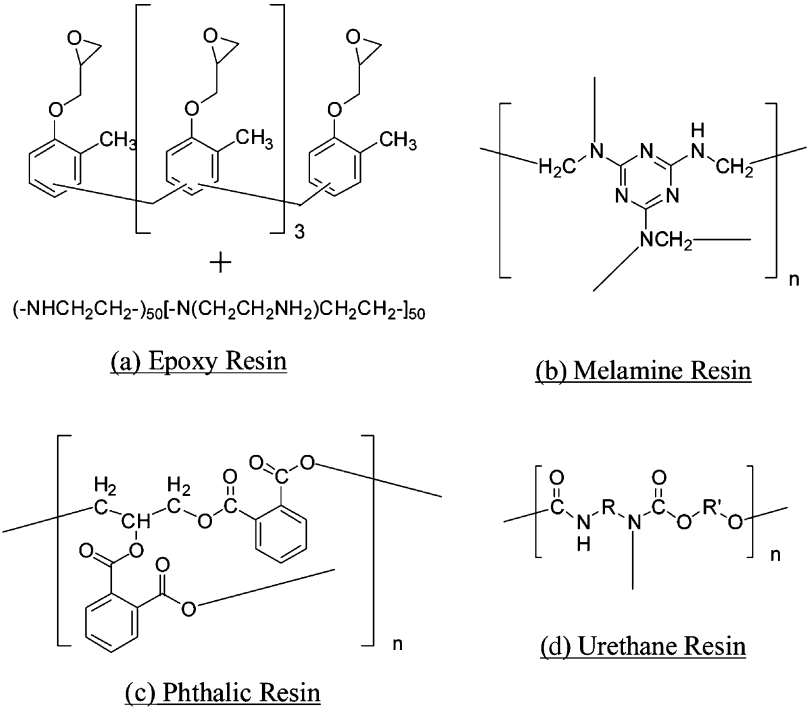

Figure 6.
Typical chemical structures of (a) epoxy resin, (b) melamine resin, (c) phthalic resin, and (d) urethane resin.

of nanomembranes toward biomedical applications, designed transport of ions and molecules, and separation purposes.

Essentially the same results were obtained when the zirconia component was replaced with silica. The SEM top view of Figure 4a shows that the pores of ANODISC (pore size, 200 nm and smaller) are fully covered with the nanofilm without any defects or cracks. TEM observation was performed on IPN nanofilm that were transferred onto a Cu grid. (Figure 4b) A smooth amorphous surface is formed, and the organic and inorganic components are both amorphous and appear to be molecularly uniform, at the SiO_2 content of around 35 mol%. This is contrasting with the presence of a regular zirconia lattice at a similar content.

Concluding Remarks

The nanomembranes as described above possess several novel features as nanomaterial. Nanomaterials may be classified as nanodot, nanowire and nanolayer, depending on the number of nano-dimensions. Nanolayer is characterized with only one nano-dimension, the other two dimensions being macroscopic. Nanomembrane is defined as being self-supporting, in addition to the intrinsic nanolayer property. The nanometer thickness provides versatile possibilities in materials separation. Reverse osmosis and the electrolyte membrane in fuel cell are typical examples. The thickness that approaches that of biomembrane will also facilitate construction of molecular devices in which individual molecules play vital roles. Design of novel molecular systems will become a reality.

[1] G. Decher, In: *Comprehensive Supramolecular Chemistry*, Vol. 9, J. L., Atwood, J. E. D., Davies, D. D., Macnicol, F., Vögtle, J-. M. Lehn, (Eds.), Pergamon, Oxford **1996**, pp 507–528.

[2] F. Caruso, R. A. Caruso, H. Möhwald, *Science* **1998**, *282*, 1111.

[3] S. M. Marinakos, D. A. Shultz, D. L. Feldheim, *Adv. Mater.* **1999**, *11*, 34.

[4] M. Onda, Y. Lvov, K. Ariga, T. Kunitake, *J. Ferment. Bioeng.* **1996**, *82*, 502.

[5] W. T. S. Huck, A. D. Stroock, G. M. Whitesides, *Angew. Chem., Int. Ed.* **2000**, *39*, 1058.

[6] A. A. Mamedov, N. A. Kotov, *Langmuir* **2000**, *16*, 5530.

[7] C. Jiang, V. V. Tsukruk, *Adv. Mater.* **2006**, *18*, 829.

[8] S. S. Ono, G. Decher, *Nano Lett.* **2006**, *6*, 592.

[9] Y. Ma, J. Sun, J. Shen, *Chem. Mater.* **2007**, *19*, 5058.

[10] I. Ichinose, H. Senzu, T. Kunitake, *Chem. Lett.* **1996**, *25*, 831.

[11] I. Ichinose, H. Senzu, T. Kunitake, *Chem. Mater.* **1997**, *9*, 1296.

[12] E. R. Kleinfeld, G. S. Ferguson, *Mater. Res. Symp. Proc.* **1994**, *351*, 419.

[13] M. Hashizume, T. Kunitake, *RIKEN Rev.* **2001**, *38*, 36.

[14] M. Hashizume, T. Kunitake, *Langmuir* **2003**, *19*, 10172.

[15] M. Hashizume, T. Kunitake, *Soft Matter* **2006**, *2*, 135.

[16] V. Richard, S. Onoue, A. Nakao, T. Kunitake, *Nature Materials* **2006**, *5*, 494.

[17] R. Vendamme, T. Ohzono, A. Nakao, M. Shimomura, T. Kunitake, *Langmuir* **2007**, *23*, 2792.

[18] H. Watanabe, T. Kunitake, *Macromolecules* **2007**, *40*, 1369.

[19] H. Watanabe, T. Kunitake, *Adv. Mater.* **2007**, *19*, 909.