Organized arrays of nanostructures in freely suspended nanomembranes

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DOI: 10.1039/b510716d

This paper gives an overview of our recent work on freely suspended layer-by-layer nanomembranes containing organized arrays of nanostructures such as carbon nanotubes or gold nanoparticles. These unique organized arrays toughen the membrane and add interesting optical properties which are useful in sensor applications. Gold nanoparticle encapsulated nanomembranes were characterized by surface enhanced Raman scattering, while those filled with carbon nanotubes were examined by resonance Raman scattering. Issues that are important to the fabrication, characterization, and applications of freely suspended polymer nanomembranes containing functional nanostructure arrays are discussed.

1. Introduction

Membranes have been widely applied in various scientific fields as, for example, biomembranes, and filtration membranes. Freely suspended membranes are key parts of microelectromechanical systems (MEMS) as sensing elements or as actuators for transferring the mechanical deflections to electrical signals and *vice versa*. These membranes are usually manufactured from silicon, ceramic, or other inorganic materials. For sizes in the millimetre range, fairly high sensitivity can be obtained with these inorganic membranes.[1] However, further minimization requires softer membranes, therefore, composite materials having low stiffness should be considered. Recently, freely suspended nanocomposite membranes combining nanostructures with a polymer matrix have shown potential in the development of microsensors and actuators, and have been the subject of ongoing interest by scientists from various fields.[2–4] These nanocomposite membranes, also known as nanomembranes, have an overall thickness of less than 100 nm. The functional nanostructures are sandwiched between the polyelectrolyte multilayer matrix, which plays an important role in the overall optical, mechanical, electronic, and other properties. These ultra-thin, freely suspended membranes are expected to replace inorganic membranes in micro- and nanodevices, while retaining high stability and sensitivity.

Layer-by-layer (LbL) assembly of multilayer films is becoming one of the most popular methods for fabricating freely suspended nanomembranes.[5–8] The advantage of the LbL method is that the resulting nanocomposite membranes can contain various nanostructures, such as carbon nanotubes, nanoclays, metal nanoparticles, and magnetic nanoparticles, giving unique mechanical, optical, or electronic properties.[9–13] For example, Kotov and co-workers reported a synthetic pathway to artificial nacre by the sequential deposition of polyelectrolytes and clays, achieving a tensile strength approaching that of natural nacre.[6] Moreover, a recent study[14] has demonstrated that the organized multilayer structure allows great scope for optical tuning. The spin-assisted LbL assembly method, introduced recently, makes the fabrication process of freely suspended nanomembranes more time efficient and easy to industrialize.[4,15,16]

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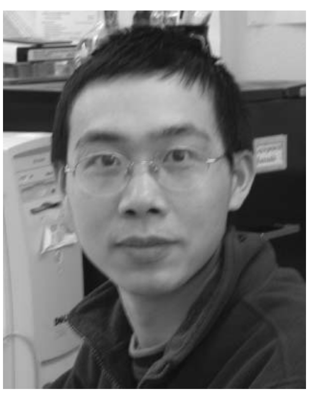

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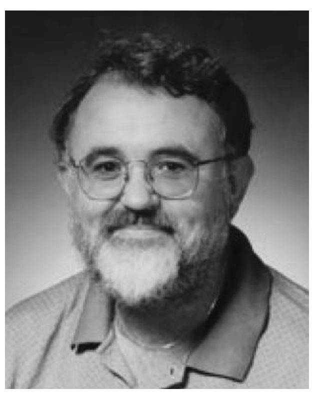

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LbL assembly allows precise control of the in-plane composition of the nanomembrane by either lithographic patterning or microcontact printing.[17,18] Using polymer-on-polymer stamping (POPS), Hammond and co-workers fabricated micropatterned LbL films on substrate surfaces.[19,20] Lvov *et al* created free-standing microcantilevers having complex shapes using a combination of photolithography and LbL.[21] The ability to tune the in-plane composition in LbL films on the micrometre and submicrometre scale is a powerful tool for the synthesis of nanoscale membranes having unique, anisotropic physical properties. These nanomembranes are expected to be highly sensitive to external stimuli and the anisotropic properties could be valuable for directional acoustic detection, optical gratings and other optomechanical applications. However, until now, there have been few reports about long range microarrays of nanostructures embedded in freely suspended multilayer polymer membranes.[15,16]

Here we present an easy and efficient method for preparing arrays of nanostructures in freely suspended nanoscale multilayers.[15,16] Our approach combines microcontact printing and spin-assisted LbL (SA-LbL) assembly with sacrificial layer methods. We have used two different types of nanostructure, carbon nanotubes and gold nanoparticles. Both can be used as fillers to toughen the nanomembrane. Gold nanoparticle filled nanomembranes were characterized by surface enhanced Raman scattering, while those filled with carbon nanotubes were examined by resonance Raman scattering.

2. Fabrication and characterization

Polyelectrolytes including poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrene-sulfonate) (PSS) were purchased from Aldrich and used without further purification. Single-walled carbon nanotubes (CNTs) produced by the arc discharge method were obtained from Carbolex (Texas, USA). A stable dispersion of CNTs in aqueous solution was prepared according to the usual procedures including oxidation, centrifugation, and filtration.[15] Gold nanoparticles were synthesized by a known procedure detailed elsewhere,[16,22] in which the $HAuCl_4$ was reduced by sodium citrate. Both CNTs and gold nanoparticles are inherently negatively charged and so can be used for electrostatic LbL assembly.

The freely suspended nanomembranes containing nanostructure arrays were fabricated by a combination of SA-LbL assembly and micro-contact printing with the sacrificial layer method.[15] The multiple steps for nanomembrane fabrication are shown in Fig. 1. First, the substrates were spin-coated with a sacrificial layer of cellulose acetate (CA). Then, the multilayers of polyelectrolytes were made from 0.2% polymer solutions by SA-LbL assembly. For the fabrication of gold nanoparticle arrays, the PAH solution was used as an ink and printed onto the polymer surface with the PDMS stamp, as reported previously.[15] The citrate-reduced gold nanoparticles were strongly adsorbed onto the PAH strips so that organized arrays of gold nanoparticles could be obtained. The method was modified when we deposited CNT arrays onto polyelectrolyte multilayers. Sacrificial polystyrene (PS) micropatterns were deposited onto the polymer surface by micro-contact printing. After the deposition of CNTs onto the PS patterned surface, the PS layer was dissolved in toluene. With this method, only those CNTs directly attached to the PAH layers remain on the membrane. After patterning the arrays, the additional polymer multilayers were deposited so that the nanostructures were encapsulated by the polymer matrix. The nanostructure multilayer was released by dissolving the sacrificial CA layer in acetone solution. The nanomembranes were transferred to copper plates having a 150 μm hole opening. The membranes were extremely thin, usually within 30–100 nm, so they could be easily ruptured and crumpled. Therefore, successful transfer of the nanomembrane required great care and patience. Once the transfer was complete, the freely suspended nanomembranes containing patterned arrays were quite stable and could be stored for months under ambient conditions.

The morphology and thickness of the nanomembranes were studied by atomic force microscopy (AFM) on a Dimension 3000 Nanoscope (Digital Instruments) in tapping mode. The mechanical properties were investigated by bulging tests, in which the over pressure was applied to one side of the membrane. The pressure was measured with the DPM-0.1 digital pressure module (SI Pressure Instruments Ltd.) to an accuracy of 2 Pa. The membrane deflections were monitored by a home-built interferometer with a helium–neon laser (632.8 nm). Raman mapping and spectroscopy were conducted on a custom-designed confocal Raman instrument. Laser light from a Nd:YAG laser (532 nm) was used to excite the sample and the Raman spectra were recorded with a SpectraPro SP-2558-W (Roper Scientific) Spectrograph and a Spec-10 : 2 KB charge-coupled device (CCD) camera.

3. Mechanical properties and Raman spectroscopy

The morphology and dimensions of the nanomembranes containing arrays of nanostructures were obtained by AFM (Fig. 2). In both images, nanostructure patterns having clear edges can be observed. Slight differences in the patterning processes meant that a few gold nanoparticles were adsorbed between the gold-enriched strips, while no carbon nanotubes were observed between the carbon nanotube-enriched strips.[15,16]

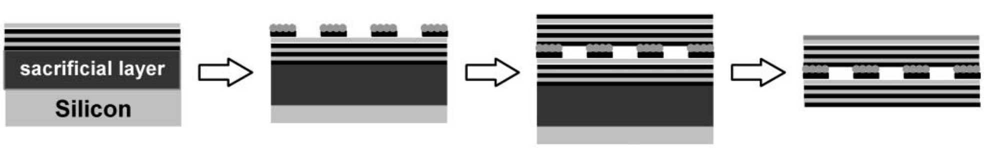

Fig. 1 Schematic of the fabrication of a nanomembrane containing patterned arrays (not to scale).

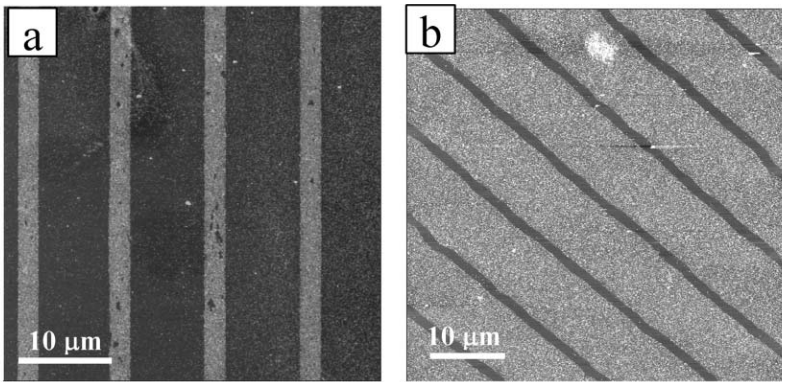

Fig. 2 AFM images of arrays of gold nanoparticles and carbon nanotubes on the surface of polyelectrolyte multilayers, (a) gold nanoparticles (reprinted with permission from ref. 16, copyright 2005 Wiley-VCH), (b) carbon nanotubes (reprinted with permission from ref. 15, copyright 2005 The American Chemical Society).

The gap between the patterned strips can be filled by the additional deposition of the polyelectrolyte. The surface of the membrane can become smooth again, depending on the depth of the gap and the number of the polyelectrolyte layers. The total thickness of the freely suspended nanomembranes was less than 100 nm, and this can be changed by the number of polymer bilayers used.

As the elastic moduli of carbon nanotubes and gold nanoparticles are much larger than those of polyelectrolytes, these fillers can efficiently enhance the mechanical properties of the nanomembrane. This was demonstrated by the bulging tests reported in our previous articles.[15,16] The results were quite close to the theoretical predictions of the Takayanagi model.[15,16] The volume fraction of nanostructures in the nanomembranes containing patterned arrays is lower than in those containing continuous layers of fillers, so the enhancement of the mechanical properties is also less.[15] Our studies showed that we can fabricate freely suspended nanomembranes, encapsulating nanostructure arrays, with excellent mechanical properties and, additionally, new anisotropic behavior. Anisotropic mechanical responses are expected for these nanomembranes and are currently under investigation.

The patterned arrays in the nanomembranes add interesting optical properties as shown by Raman scattering behavior. Confocal Raman mapping of the patterned carbon nanotube nanomembranes gave excellent Raman intensity contrast caused by resonance Raman scattering from the carbon nanotube area. Fig. 3a shows the intensity distribution of the 1590 cm^{-1} Raman mode (G-line of carbon nanotube), in which parallel lines are separated by narrower dark gaps having a period of 10 μm. The gold nanoparticle arrays gave rise to a strong periodic modulation in the Raman spectra, shown in Fig. 3b, caused by the tremendous differences between different areas of the patterned membrane. The large enhancement of the Raman signal makes direct study of the microstructure in the ultrathin nanomembrane possible.[23] Our recent results of *in situ* SERS investigation, deflecting freely suspended nanomembranes, revealed a two-stage molecular mechanism during the deformation process due to the pressure differential.[23] Based on these experimental data, we suggest that bridging polyelectrolyte chains between the inorganic nanostructures can produce an effective toughening mechanism, resulting in outstanding mechanical strength and recovery.[23]

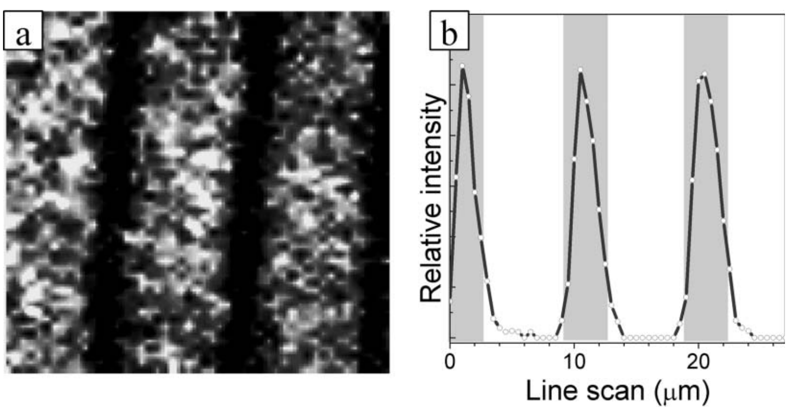

Fig. 3 Raman scattering from nanomembranes containing Au/CNT nanostructure arrays. (a) Raman mapping of the G-line of carbon nanotube patterned nanomembranes, area 30 × 30 μm. Reprinted with permission from ref. 15, copyright 2005 The American Chemical Society. (b) The intensity variation of the SERS signal across several strips of the gold nanoparticle array (reprinted with permission from ref. 16, copyright 2005 Wiley-VCH).

4. Conclusions and outlook

We showed that microarrays of nanostructures in freely suspended nanomembranes can be fabricated by combining spin-assisted LbL assembly, microcontact printing, and the sacrificial layer method. So far, we have succeeded in assembling arrays of carbon nanotubes and gold nanoparticles in ultra-thin multilayer membranes. Our approach is novel and versatile, and can be extended to other functional nanostructures. The freely suspended nanocomposite membranes, having unique nanoscale organized structures, possess interesting optical and mechanical properties useful for highly responsive sensors and other MEMS applications.

There are several interesting questions relating to the fabrication and application of nanoscale membranes containing arrays of nanostructures. The first is the minimum achievable thickness for a stable freely suspended nanomembrane. So far, with PAH and PSS polyelectrolytes, we have successfully made a freely suspended multilayer film with a thickness as low as 30 nm.[4] The bending stiffness is proportional to the third power of the film thickness, so the nanoscale thin film can be easily crumpled. One possible solution is to use crosslinkable polyelectrolytes. By chemical crosslinking, the nanomembrane will be much stronger and more stable. For example, ultrathin Langmuir films have been reported[24] which are quite stable after crosslinking. Freely suspended multilayers have also been reported[25] with crosslinking, but this has not been applied to membranes containing patterned arrays.

A further experimental challenge is in-plane orientation of the nanostructures inside the microarrays. We have demonstrated that it is possible to align the carbon nanotubes by using the appropriate fabrication technique.[26] The orientation of the nanostructures inside the arrays is expected to greatly enhance the physical properties of the nanomembranes in certain directions. Additional anisotropic behavior might be expected from the in-plane nanoscale orientation in the micro-arrays. Anisotropic properties provide an easy way to tune the properties of the nanocomposite in different directions, and could be valuable for their application in direction-sensitive detectors.

Further detailed characterization of freely suspended nanomembranes containing patterned arrays is important. We have already made some investigations of their morphology, mechanical properties, and Raman spectra. Recently, we reported that the chain alignment in the nanomembrane can be monitored with SERS on the gold nanoparticle surface.[23] Since both the gold nanoparticles and carbon nanotubes are electronically active, our nanomembranes with arrays of gold nanoparticles or carbon nanotubes are expected to have interesting electronic properties, such as anisotropic conductivity. The use of the gold nanoparticle LbL films as gas sensing membranes has been reported.[11] More experiments on the electronic properties are under consideration and the sensing properties will be explored. Futhermore, incorporation of magnetic nanoparticles into the freely suspended nanomembranes will add interesting magnetic properties. All of these unique properties will be valuable for their application in various sensors, including, but not limited to, directional acoustic sensors, trace chemical detectors, tunable optical gratings, and optomechanical sensors.

Acknowledgements

The authors thank Hyunhyub Ko, Hennady Shulha, Sergiy Markutsya, and Wilber Y. Lio for their work on sample preparation and characterization. This work is supported by NASA through the NDE center contract NAG 102098, AFOSR, F496200210205, and AFOSR-DURIP F49620-03-1-0273 grants.

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