NANOCOMPOSITE FREE-STANDING STRUCTURES WITH ENCAPSULATED NANOPARTICLES

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Introduction

In this presentation we will focus on recent developments in SEMA research group on designing, fabrication, and characterization of free standing flexible nanocomposite structures fabricated with spin-assisted layer-by-layer (LbL) assembly [1]. A major focus will be on new types of flexible freely-standing nanostructures with encapsulated highly oriented silver nanowires, quantum dots, 3D sculptured LbL films from conjugated polyelectrolytes, layered hydrogels with encapsulated gold nanorods, as well as highly perforated LbL nanomembranes.

Sculptured LbL films

First, we discuss freely standing, three-dimensional, layer-by-layer (LbL) films with the microscopic periodic modulations of refractive properties.[2] The modulated refractive properties are achieved by the topological variation of the film shape that generates optical diffraction effects with bright structural colors and optical grating properties. An LbL deposition of conjugated polyelectrolytes on a sacrificial microimprinted substrate was employed to generate such a sculptured LbL structure with the effective thickness of 60 nm and the 160-nm peak-to-peak modulation (Figure 1).

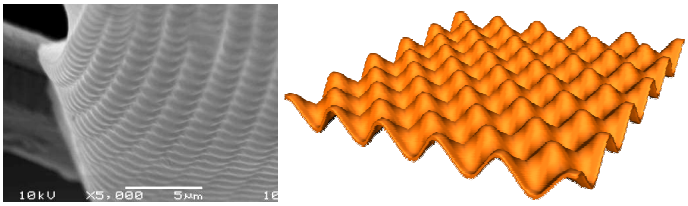

Fig. 1. SEM image of sculptired LbL film and corresponding schematics.

The modulated refractive properties achieved by the topological variation of the LbL film shape can generate intense structural color effect with bright structural colors and optical grating properties, a phenomenon which can be of interest for light-controlling polymeric microdevices and free-standing nanoscale flexible membranes and films.

Nanoperforated membranes

Ultrathin, nanoperforated, and freely-suspended membranes with uniform nanopores in the range of tens of nanometers have been fabricated using LbL assembly on hydrophobic substrates.[3] Membranes with thicknesses down to 20 nm displayed highly perforated morphology (Figure 2) and were robust enough to be released from the sacrificial substrates, transferred onto various surfaces, and suspended over microscopic openings. The nanopore size can be controlled by tuning the number of polyelectrolyte bilayers, spinning speed, and a proper selection of sacrificial hydrophobic substrates.

We demonstrate that the formation of nanopores is caused by partial dewetting of polyelectrolytes layers in the course of their deposition on the underlying hydrophobic surfaces. Nanoscale thickness of perforated membranes with relatively uniform size and high concentration of nanopores provide perspectives for higher rates of transport through freely suspended LbL membranes and the overall design suggests an intriguing combination of nanopores, nanoscale membrane thickness, and easy functionalization of both surfaces.

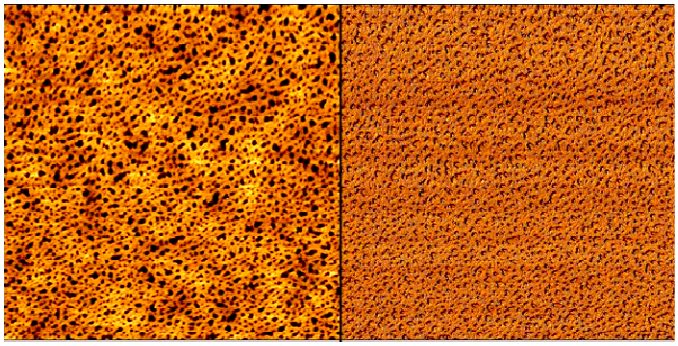

Fig. 2. AFM image (topography and phase) of nanoperforated LbL film.

pH responsive LbL hydrogels

We suggested a straightforward fabrication of the optically responsive ultrathin membranes useful for monitoring

membrane swelling/de-swelling changes in the biologically important pH range from 5 to 8. The ultrathin, 55 nm-membranes were fabricated by inclusion of the gold nanorods into the swollen cross-linked $(PMAA)_{20}$ LbL hydrogel films through electrostatic interactions (Figure 3).[4]

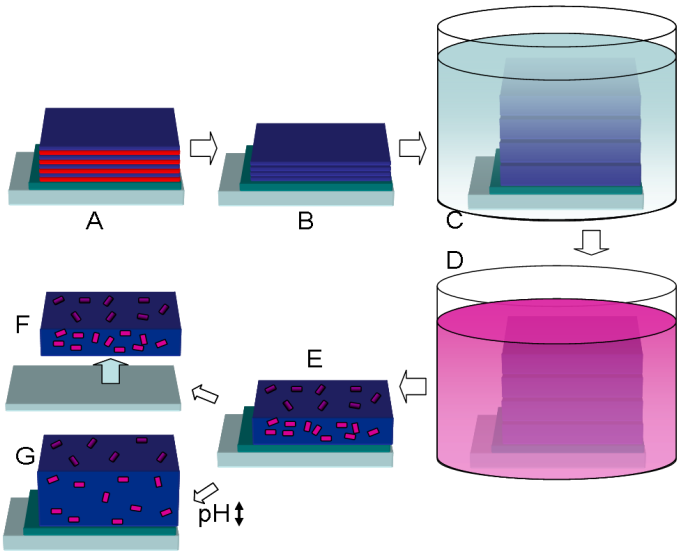

Fig. 3. Schematics of fabrication of layered hydrogels with gold nanorods.

We demonstrated that the gold nanorods with controlled density can be loaded into LbL hydrogels (Figure 4). In contrast to the majority of the sensing methods with nanoparticles reported in the literature which rely mostly on the quenching effects when the intensity decrease is monitored upon the environmental change event, pH-induced swelling/de-swelling of the reported (PMAA-Au NRs)$_{20}$ membranes can be easily tracked by monitoring shifts in the longitudinal SPR peak of gold nanorods. We show that pH-induced de-swelling of the (PMAA-Au NRs)$_{20}$ film causes a significant blue-shift of the plasmon band by 21 nm, which reflects an increase in the refractive index within the hydrogel film with the pH decrease from 8 to 5.

We suggest that the longitudinal SPR peaks of gold nanorods is more suitable for monitoring pH-induced changes within the membranes than the transverse SPR bands for nanorods or for gold nanoparticles due to its stronger intensity and higher sensitivity to the environmental conditions. Importantly, due to the stronger interactions among gold nanorods within highly-loaded hydrogel films the substrate pre-coating with gold is not required to yield large SPR response to pH changes.

In contrast with most of known pH responsive materials which rely on pH-triggered change in the intensity of photoluminescence or plasmon bands, the responsive structures suggested here cause pH-triggered and very significant shift in easily detectable plasmon resonance bands. Additionally, it is worth noting that these ultrathin hydrogel films are strong enough to be released from the substrates yielding free-floating films and thus they can be utilized as stand-alone pH responsive membranes. Moreover, these hydrogel LbL films can be further transferred to other microfabricated supports and utilized in a variety of sensing applications.

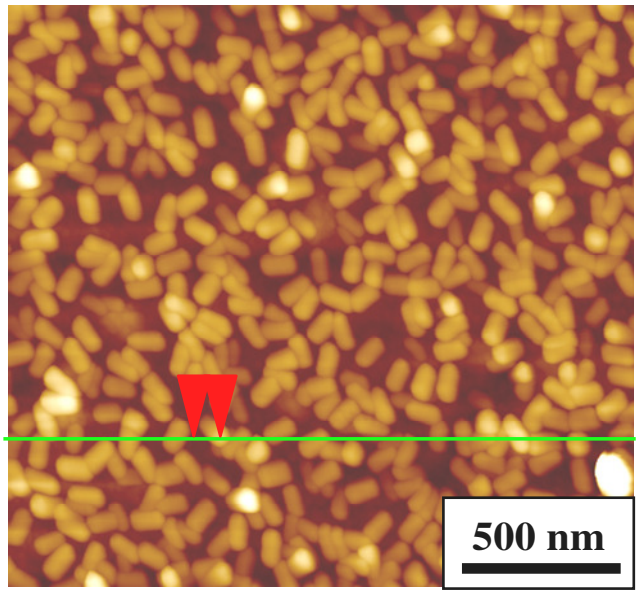

Fig. 4. Gold nanorods load inside LbL hydrogel films.

Acknowledgements

The results reported here have been obtained by students and post-docs in VVT group: C. Jiang, D. Zimnitsky, R. Gunawidjaja, YH Lin, V. Kozlovskaya, and V. V. Shevchenko. This work is supported by AFOSR and NSF-NIRT-0506832 Grants.

References

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