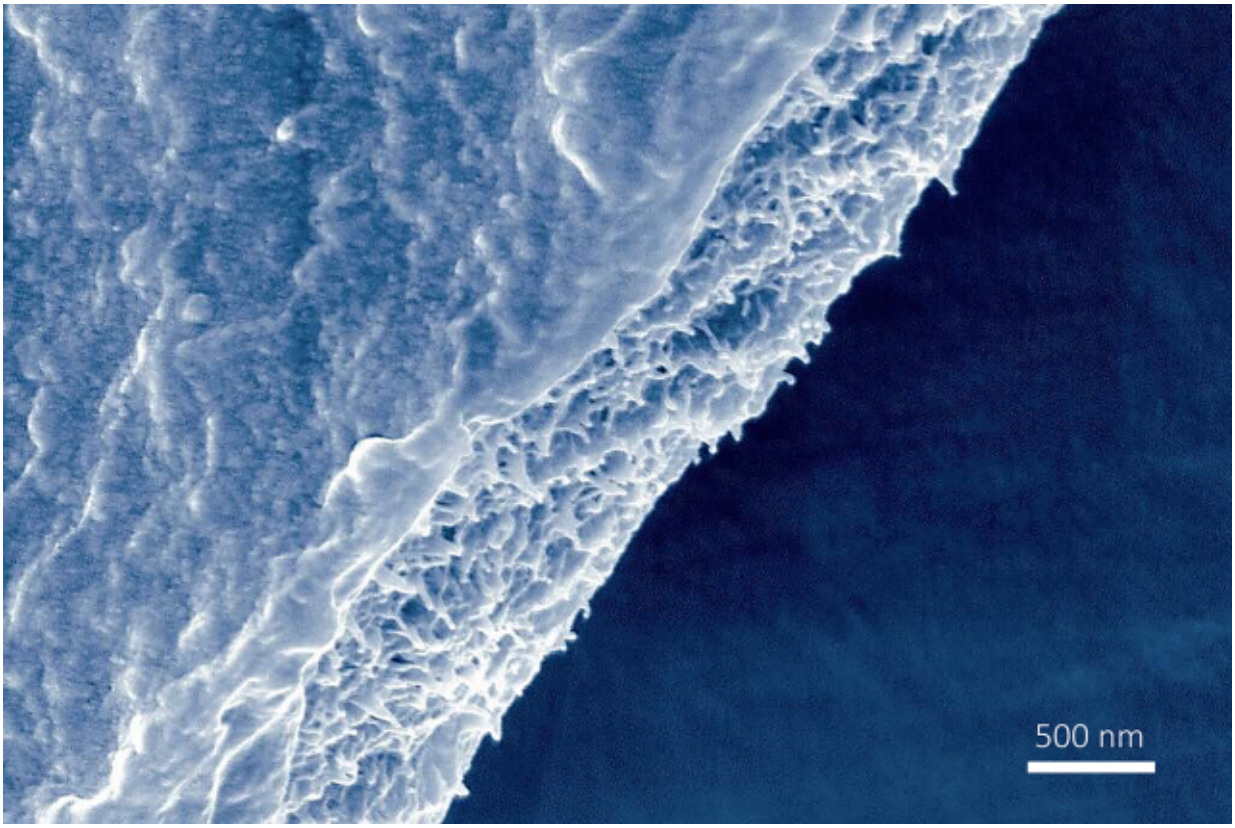
Silk-based filtration material breaks barriers

June 24 2016, by Marilyn Siderwicz



A scanning electron micrograph shows a free-standing Bombyx mori silk nanofibril membrane. Credit: Massachusetts Institute of Technology

When the Chinese first discovered silk, its superior quality and properties were thought so special, it was reserved exclusively for clothing the emperor, his relatives, and dignitaries. And for more than two millennia, the mechanisms of silk production were a highly guarded

secret.

Fast forward to today: MIT and Tufts University researchers have discovered additional hidden secrets of silk, called nanofibrils, which, when expertly extracted and reassembled, can be manufactured into advanced filtration membranes. The researchers' new silk-based filtration technique was recently described and published in the paper, "Ultrathin Free-Standing Bombyx mori Silk Nanofibril Membranes" in the journal *Nano Letters*.

The paper reveals how silk nanofibrils (SNFs), a key nanocale building block of natural silk, can lead to new naturally-based filters that are more effective, less expensive, and "greener" compared with traditional commercial products. This discovery could portend new production methods and supply chain economics for anyone that uses the new filter membranes, including water treatment facilities, food manufacturers, and life sciences organizations.

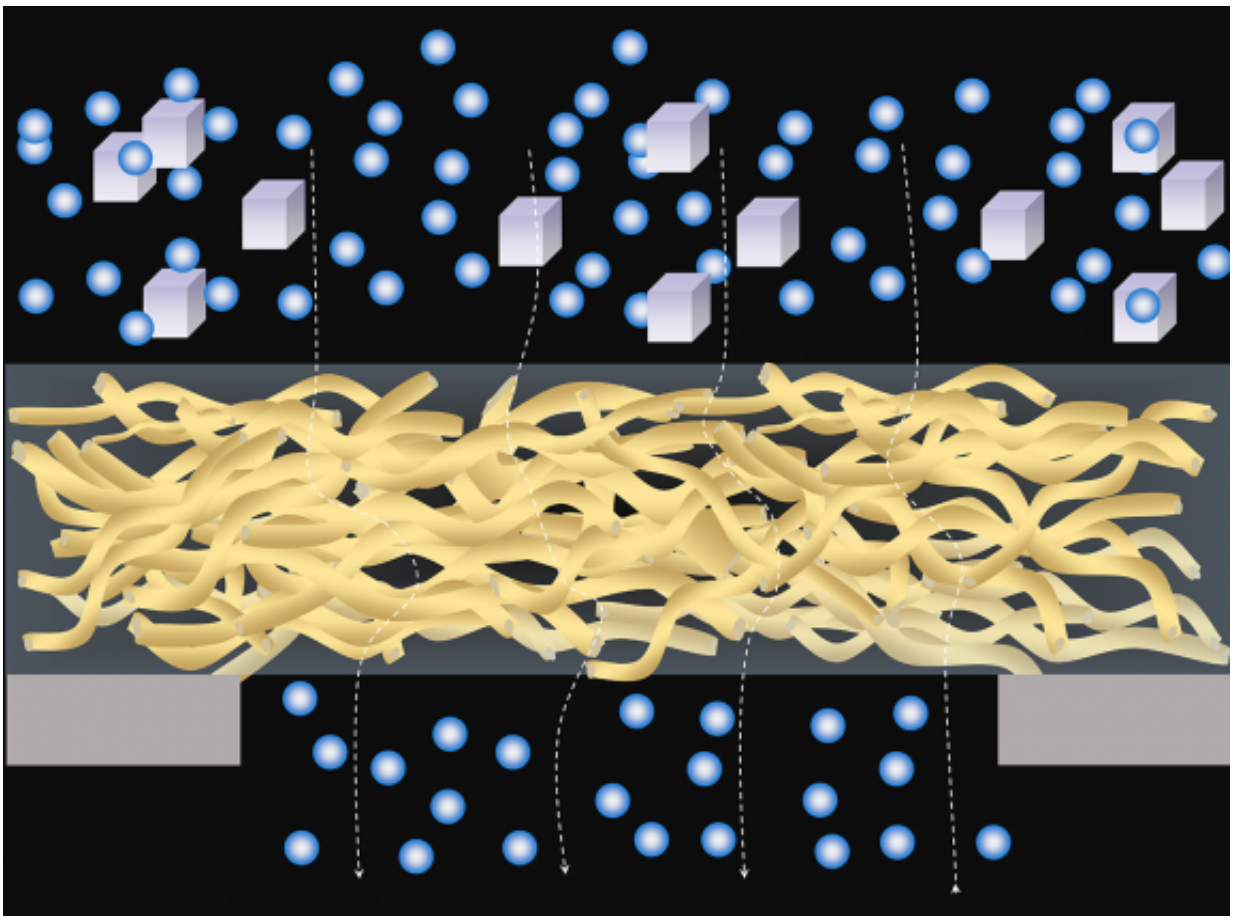
The researchers included Department of Civil and Environmental Engineering (CEE) graduate student Kai Jin; CEE postdoc Shengjie Ling; Markus J. Buehler, head of CEE and the McAfee Professor of Engineering; and Professor David L. Kaplan, chair of the Tufts Department of Biomedical Engineering.

"There has been a renewed focus recently on developing these types of ultrathin filtration membranes which can provide maximum flow-through while retaining molecules or pollutants that need to be separated from the flow," Ling says. "The challenge has always been to create these new ultrathin and low-cost devices while retaining mechanical strength and good separation performance. Cast silk fibroin membranes aren't an option, because they do not have porous structure and dissolve in water if not pretreated. We knew there had to be a better way."

An insurmountable challenge—until now

The researchers spent many months sharing ideas, working and reworking calculations, and experimenting in the lab. Their effort to find just the right solvent to dissolve the silk fibers into their most elemental compounds without destroying the samples was one of their greatest challenges.

"We devoted a lot of time developing the method for extracting the nanofibrils from the natural silk fibers," Ling says. "It's a novel approach, so we had to use trial and error before we eventually found success. It was such a good feeling to realize in tangible results what was calculated."



This illustration demonstrates how silk nanofibril membranes (yellow) reject large molecules while allowing small molecules to pass through. Credit: Massachusetts Institute of Technology

Their work—a collaborative effort among civil, biomedical, and computational engineering, and materials science—found the solution in this new free-standing ultrathin filtration membrane and its innovative, advanced production technique.

Infinitesimal, but mighty

Natural silk fibers, which are made of pure protein, are renowned for their incredible lightness, strength, and durability. The silk nanofibrils used by the researchers were exfoliated from domesticated silkworm-produced fibers. It is the special character of the silk nanofibrils that helps the innovative membranes retain their exquisite structure and superior physical properties.

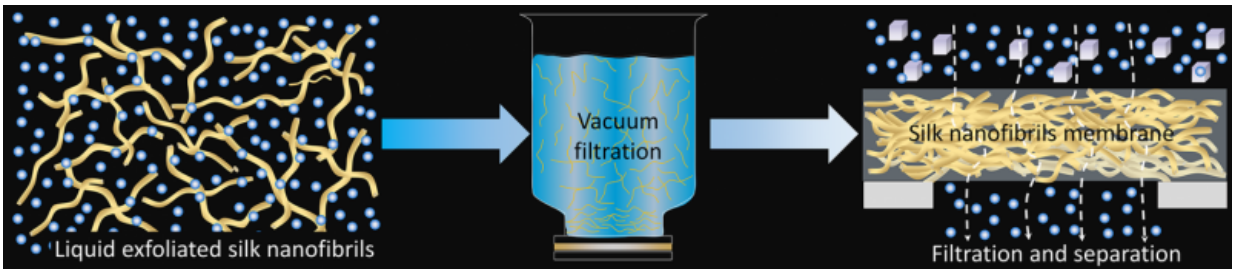
Historic methods to extract or prepare these nanofibers have not always worked. The illustration in the slideshow above shows the researchers' unique four-step approach that proved effective by overcoming prior hurdles. The first two steps were used to exfoliate the silk nanofibrils from the silk fibers by degumming, washing, drying, and incubating them at a constant temperature, before placing them in water and stirring or shaking them to remove any undissolved silk. The third step involved using ultrasonic waves to extract the silk nanofibrils, which remained stable over several months. Scanning electron micrograph imagery showed the silk nanofibrils had a diameter and contour length similar to the diameter of a single nanofibril strand. In the last step and final

process, they assembled the silk nanofibrils into the ultrathin membranes using a vacuum filtration process.

Success came in meeting and exceeding three important membrane attributes: thickness (40-1,500 nanometers with narrowing pore sizes of 12-8 nm); superior water permeation, known as flux; and excellent broad-spectrum separation performance for most dyes, proteins, and nanoparticles. All of these mechanical superiority results are critical to industry, especially for use in pressure-driven filtration operations, even at high applied pressures.

Whether purifying waste water for drinking, or capturing the minuteness of blood clots in the human body, these new silk-based membranes offer significant advanced operational efficiencies. And one piece of silk nanofibrils membrane averages only $0.05-$0.51 compared with $1.20 per piece of commercial filtration membrane.

Silk nanofibrils used in manufacturing hold other important benefits, too. As the by-products of silkworms, innovative manufacturers who leverage silk's natural properties can enhance their industrial ecology and produce less environmental stress. And once the filters are replaced, the used ones biodegrade, leaving no lasting impact.



This illustration shows a new ultrathin filtration membrane prepared from silk nanofibrils (SNFs) that are directly exfoliated from natural Bombyx mori silk

fibers. Credit: Massachusetts Institute of Technology

A keen eye for detail

Controlling the thickness of membranes and pore size distribution is especially important for filters to work effectively, so the researchers made sure the interconnected membrane pores produced in the lab were uniform and without cracks or pinholes.

In addition, they noted the new membrane's rejection of protein and gold nanoparticles in flow was higher than that of membranes with similar thickness. Protein molecules, colloids, nanoparticles, small molecules, and ions were all used to assess size-selectivity.

The researchers experimented frequently with water fluxes through membranes of different thicknesses (40-60 nm).

"What really surprised us," says Jin, "is that one flux was faster than that of most commercial materials, in fact, more than 1,000 times higher in some cases." The result proved better than fluxes of the most advanced ultrathin membranes.

Other findings showed remarkable flexibility, ease of use and sustainability. For example, the new membranes could be removed without adhering to the supporting substrate, they appeared homogeneous, were transparent with structural color on the surface, could be cut and bent without damage, and probably most important, did not dissolve in water—a critical role in most filtration processes. And because silk nanofibrils are negatively charged at neutral pH, more positively charged molecules can be taken up by the membranes via electrostatic interactions.

"These natural silkworm membranes have remarkable separation efficiency on par with current synthetic technologies," says Professor Kristie J. Koski of Brown University's Department of Chemistry, who was not involved in the research. "As a non-toxic, flexible, and tunable membrane, they have great potential for purification and recycling especially in applications where synthetic alternatives are not an option such as in biological systems."

Professor Thomas Scheibel of The University of Bayreuth in Germany, who also was not associated with the study, adds: "The filter efficiency is one of the most important parameters of filter materials. This parameter is mainly influenced by the structure of the filter material. Nano silk filters are consistently filled and therefore enable the retention of quite small particles. New filter devices based thereon should allow lowering the overall energy consumption in water as well as in air filtration at constant or even higher filter efficiencies than existing ones."

The team's discovery reflects ways in which silk's hidden secrets can advance civilization in multiple new ways.

More information: Shengjie Ling et al. Ultrathin Free-StandingSilk Nanofibril Membranes, *Nano Letters* (2016). DOI: 10.1021/acs.nanolett.6b01195