Cellulose: An ever-present material with remarkable properties

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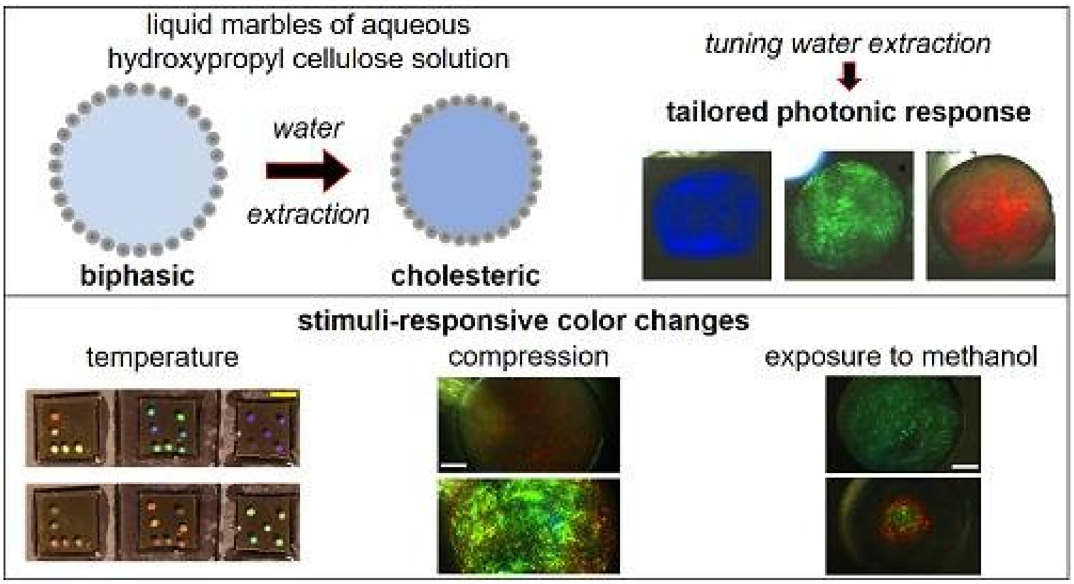


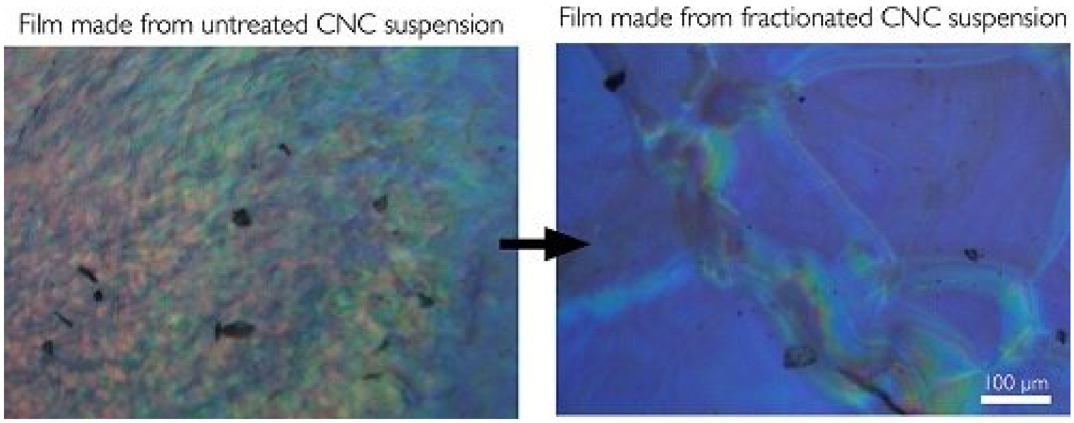
Credit: University of Luxembourg

Physicists from the University of Luxembourg have recently made significant steps forward in resolving some of the outstanding research questions about cellulose. Their findings have been published in the prestigious journals *Angewandte Chemie* and *Communications Materials*.

Cellulose is everywhere

What do your jeans, broccoli, paper, trees in the forest and one of the hottest nanoparticles in current international materials research have in common? As unrelated as these items may appear at first sight, they are all made of the polymer cellulose. It is actually not so surprising that cellulose appears in so many contexts, because it is the single most abundant polymer on earth, synthesized in every plant in order to give it strength and structure. Since ancient times, humankind has understood to use this amazing material, turning it into paper for writing on, cotton fibers for making clothing, and during the industrial age into related materials like cellophane for packaging, nitrocellulose for nail polish and photographic film, or hydroxypropylcellulose (HPC) for creating the shape and volume of the pill that you take when you need to get a few milligrams of medicine. While HPC makes up about 99% of the pill, this is not digested, just like we cannot digest the natural cellulose in broccoli when we eat it. Yet, that cellulose is crucial in ensuring that our intestines work well; what is often referred to as 'fiber' in food is nothing but cellulose.

Today, cellulose as an advanced material is going through a rebirth, as scientists around the world, in universities as well as in industry, are discovering new ways of taking advantage of its remarkable properties. This new development is based on the recognition that cellulose and derivatives like HPC can self-organize into complex ordered structures, with spectacular optical and mechanical properties, when suspended or dissolved in water under the right conditions. When cellulose enters this ordered liquid state, called a 'liquid crystal,' it opens for functional materials with a range of application opportunities, that are produced sustainably and are fully biodegradable, leaving a minimum footprint on our planet. This is because they are derived from plants, algae and other regrowing abundant raw materials. However, the processes involved are complex, and in order to get the right properties in the produced materials, many challenging—but also stimulating—questions in chemistry as well as physics have to be answered.



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Liquid crystal really matters

In two papers just published in the prestigious journals *Angewandte Chemie* and Communications Materials, respectively, the Experimental Soft Matter Physics group, led by Prof. Jan Lagerwall at the Department of Physics and Materials Science of the University of Luxembourg, presents significant steps forward in resolving some of the outstanding research questions standing between the abundant cellulose resource generously provided by Mother Nature and the advanced materials we hope to derive from it. Both papers summarize research funded by the Luxembourg National Research Fund FNR (projects COReLIGHT, SSh and MISONANCE).

In the first paper, Emmanouil Anyfantakis, postdoctoral researcher at the University of Luxembourg, and co-workers present a radically new way of processing HPC solutions, allowing them to be prepared and manipulated at low concentrations where they flow easily. Once they have acquired their target shape—here a roughly millimeter-sized sphere referred to as a "liquid crystal marble"—the concentration is increased in a very controlled way by letting excess water diffuse into a surrounding organic solvent, which can be reused after the process. The liquid crystal marbles exhibit striking optical properties thanks to the arrangement of the HPC into a helix structure with period on the same scale as the wavelength of visible light.

"Remarkably, this kind of structural color is seen throughout the whole marble, which is not what one expects for this type of liquid crystal in spherical shape, and the color can be tuned throughout the whole visible spectrum, from violet to red. We have demonstrated that the marbles can be used as non-electronic (and therefore autonomous, i.e. no battery or other power source is needed) sensors of many different stimuli, including temperature, mechanical deformation and the presence of toxic chemicals. For instance, a liquid crystal HPC marble initially prepared for green color shifts to red and finally loses its color when exposed to the toxic alcohol methanol," explains Emmanouil Anyfantakis.

In the second paper, Prof. Jan Lagerwall and his former doctoral candidate Camila Honorato-Rios, now R&D engineer at the Luxembourg Institute of Science and Technology (LIST), have focused on pure cellulose, here in the form of cellulose nanocrystals (CNCs). These are nanorods of crystalline cellulose that are a few hundred nanometres in length and some 5-10 nanometres in width. Also CNCs form a liquid crystal phase in water with the rods organizing into a helical structure. CNCs constitute one of the hottest nanomaterials today, as they are sustainably produced and can be highly useful on their own as well as in composites. Unfortunately, their production methods leave the nanorods very disperse in length, i.e., every CNC batch contains many long as well as many short rods.

"In the paper, we have shown that this length dispersity is one of the main reasons for the many problems in processing CNC suspensions and obtaining materials with uniform properties, because long- and short-rod suspensions have very different viscosities and the period of the liquid crystal helix gets shorter the longer the rod. The dispersity of lengths therefore mixes CNCs that would need to be processed on very different time scales, and when they are transferred into solid films that should benefit from the liquid crystalline order, they are broken up into mosaic-like brittle structures because of the competition between short and long rods to organize into long- and short-period helices, respectively," explains Camila Honorato-Rios.

Importantly, the authors also provide the solution. Camila Honorato-Rios and Jan Lagerwall show that the phase separation between the liquid crystal phase and an ordinary disordered liquid, spontaneously taking place in CNC suspensions, can be used to fractionate CNC suspensions according to length. By using separatory funnels, a standard component of any chemistry lab, they divide the disperse CNC suspensions into individual fractions, each of which has a much narrower length distribution. This allows them, for the first time, to study the behavior of long, medium and short CNCs individually. This way they produce solid films showing uniform and controlled structural color, without the mosaic texture. "Because the technique is easily scalable, this can be a game changer for the industrial exploitation of CNC. Following the fractionation procedure, CNC producers can provide samples with much lower dispersity, allowing customers to use this remarkable new, sustainably produced, nanomaterial in a way that maximizes its performance," comments Prof. Jan Lagerwall with enthusiasm.

More information: Manos Anyfantakis et al. Responsive Photonic Liquid Marbles, *Angewandte Chemie* (2020). DOI: 10.1002/ange.202008210

Camila Honorato-Rios et al. Interrogating helical nanorod self-assembly with fractionated cellulose nanocrystal suspensions, *Communications Materials* (2020). DOI: 10.1038/s43246-020-00069-z

Provided by University of Luxembourg