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SUPERHYDROPHOBIC AND SUPEROLEOPHOBIC NANOCELLULOSE AEROGEL AS BIOINSPIRED CARGO CARRIERS ON WATER AND OIL

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Abstract

We demonstrate that superhydrophobic and superoleophobic nanocellulose aerogels, consisting of fibrillar networks and aggregates with structures at different length scales, support considerable load on a water surface and also on oils as inspired by floatation of insects on water due to their superhydrophobic legs. The aerogel is capable of supporting a weight nearly 3 orders of magnitude larger than the weight of the aerogel itself. The load support is achieved by surface tension acting at different length scales: at the macroscopic scale along the perimeter of the carrier, and at the microscopic scale along the cellulose nanofibers by preventing soaking of the aerogel thus ensuring buoyancy. Furthermore, we demonstrate high-adhesive pinning of water and oil droplets, gas permeability, light reflection at the plastron in water and oil, and viscous drag reduction of the fluorinated aerogel in contact with oil. We foresee applications including buoyant, gas permeable, dirt-repellent coatings for miniature sensors and other devices floating on water and oil.

Introduction

Several plants and animals incorporate superhydrophobic surfaces having water contact angle CA > 150°, thus providing materials scientists exciting models for functional bio-inspired surfaces.[1-4] Classic examples are the self-cleaning leaves of Lotus plant, the non-fogging compound eyes of mosquitoes, and the locomotion of water striders on water surfaces.[1-8] Although a wealth of bio-inspired concepts have been introduced to achieve superhydrophobicity,[1-9] superoleophobic surfaces with CA > 150° for oils are rare and considerably more challenging to construct as the surface tension of oils is only a fraction of that of water.[10-15] In addition to chemical composition and roughened texture, a third parameter is essential to achieve superoleophobicity, namely re-entrant surface curvature in the form of overhangs. The overhangs can be realized as fibers,[10,12-14] mushroom-like structures[10] and pores[11,16]. Superoleophobic surfaces are appealing for e.g. anti-fouling, since purely superhydrophobic surfaces are easily contaminated by oily substances in practical applications, which in turn will impair the liquid repellency.

Result and discussion

Mechanically robust nanocellulose aerogels with a mass of 3.0 mg, diameter of 19 mm and thickness of 0.5 mm are prepared by vacuum freeze-drying. The resulting density is 0.02 g/cm^3. Taken the definition of porosity $\phi = 1-(\rho_a/\rho_s)$, where ρ_a is the density of aerogel and ρ_s is the density of crystalline cellulose (1.5 g/cm^3), the resulting porosity is 98.6%. The aerogels were fluorinated with fluorosilanes using chemical vapor deposition (CVD) (see Fig. 1D for the bottle-in-bottle setup for CVD). The unmodified aerogel contains free hydroxyl groups on the surface, which react with chlorosilanes to form a covalent Si-O bond. There are two advantages of the CVD bottle-in-bottle setup. Firstly, it avoids direct contact of the aerogel with the liquid fluorosilane. Secondly, it reacts at low temperature (70°C) so that the inherent structures and properties of cellulose aerogel do not get damaged. Without the fluorination treatment, a water droplet becomes immediately absorbed within an aerogel without any measureable contact angle. By contrast, for the fluorinated aerogel a water contact angle of 160° is observed (Fig. 2D), indicating superhydrophobicity.

Even more interestingly, high contact angles of 153° and 158° are observed for respectively paraffin oil and mineral oil (Fig. 2C), indicating additionally superoleophobicity. Note that the floatation capability of nanostructured aerogel membranes was inspired by the structures at different length scales within the water strider legs, which contain micron-sized setae and nanosized grooves that trap air due to biological surface active coatings and correspondingly the superhydrophobicity (Fig. 2A). In rough analogy, our nanocellulose membranes show structures at several length scales from nanometer scale individual nanofibers up to micronscale nanofibrous aggregates (Fig. 2B).

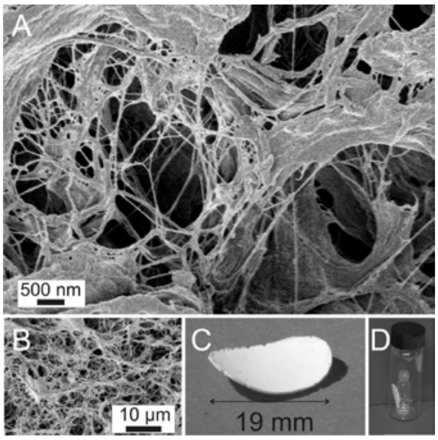

Figure. 1. (A+B) Scanning electron micrograph of native nanocellulose aerogel structure with robust network structuring at several length scales due to individual nanofibers and their aggregates. **(C)** Photograph of a nanocellulose aerogel membrane. **(D)** Bottle-in-bottle setup for fluorination by chemical vapor deposition

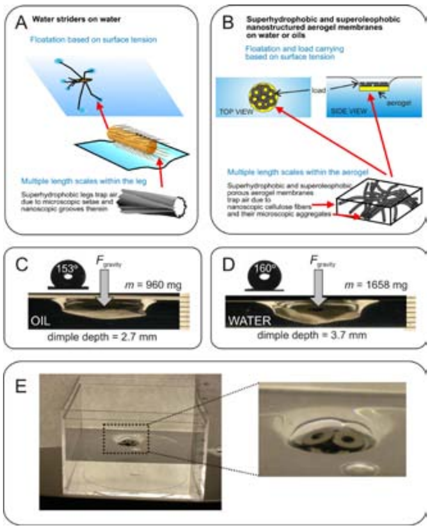

Fig. 2 Floatation and load carrying on oil and water based on fluorinated nanostructured aerogel. **(A)** Inspiration came from water striders, a class of insects capable of standing on water based on surface tension. **(B)** Cartoon of a fluorinated nanofibrous cellulose aerogel membrane floating on water and oil due to surface tension. As in water striders, also in the aerogels the topography for liquid repellency is induced by fibers, but in this case the fibers form mechanically robust entangled networks. **(C+D)** Contact angle measurement and load carrying experiment of the aerogel on respectively paraffin oil and water. The side-view photograph of the aerogel load carrier on paraffin oil and water shows the dimple at maximum supportable weight. The scale markers on the right are in mm. **(E)** Load carrying setup. Metal weights (washers) are loaded on the fluorinated aerogel membrane floating on water (similarly on oil).

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