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EDGE ARTICLE

Vapour-driven Marangoni propulsion: continuous, prolonged and tunable motion†

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We show the vapour-driven Marangoni effect as a new paradigm for the continuous self-propulsion of floating soft machines by transduction of chemical energy to motility, featuring a prolonged locomotion at steady velocity with a small amount of on-board fuel. The propulsion is induced by modification of the liquid surface using organic vapour transported through a nanocellulose aerogel membrane. The steady velocity is achieved through a continuous supply of fuel vapour that lowers the surface tension of the liquid, combined with the spontaneous recovery of the surface tension after the floating machine has passed. The membranes are gas permeable from their open-porous nanofibrillar structure and float on water and oils due to their superhydrophobic and superoleophobic nature. The velocity is tunable by selecting solvents with different vapour pressure.

Introduction

Motility is an essential quality in biology, industry, daily life, and more recently has spurred research in functional soft matter and nanodevices.[1–12] The motility mechanism may depend on a variety of factors, among which the size of the object and the source of energy play central roles. The smaller the object, the more essential becomes its surface energy as compared with body-related energies. One motility mechanism is based on the Marangoni effect,[13] namely motion induced by surface tension gradients (from low to high surface tension). Marangoni propulsion of floating objects has been demonstrated mostly using liquid[6,14,15] or solid surfactants,[16] and sporadically also using light.[17,18] A classic demonstration is given by "soap boats",[6,14,15] where a small amount of unsymmetrically applied liquid surfactant gives a momentary and uncontrolled propulsion for an object floating on water. Interestingly, in the biological world the mechanism is used by the water strider *Microvelia* and by some terrestrial insects that accidentally fall into water. They have an emergency form of locomotion on the water surface to escape from predators or to reach the bank.[6,19] These insects induce Marangoni motion by surface tension gradients upon excretion of a liquid surfactant leading to a momentary increase of speed. However, liquid-surfactant-powered Marangoni propulsion typically is one-shot and does not lead to a controlled, continuous, prolonged motion. This is so since the rate of surfactant release is usually ill-controlled, and, in addition, because the surface tension gradients quickly decay by equilibration of the interfacial surfactant. "Camphor boats", as the most typical example of solid-surfactant-powered Marangoni propulsion, can lead to prolonged motion, but require channels to confine the otherwise irregular motion and speed is not tunable.[16] For regular, prolonged and tunable Marangoni propulsion at the free liquid surface, new schemes need to be identified.

Results and discussion

Here we demonstrate the novel concept of vapour-driven Marangoni locomotion. First, a porous object capable of floating on water and oil was made based on a superhydrophobic and superoleophobic nanofibrillar membrane, *i.e.* permeable to gases but repellent for liquid water and oil.[20] The main point underlying this concept is that diffusion of vapour to the liquid interface enables easy, autonomous and continuous transport of fuel for the Marangoni propulsion. Equally important, the volatility of the gaseous Marangoni fuel would enable the restoration of the original surface tension of the carrying liquid once the object has passed this location. To achieve motility, we lowered the surface tension of the carrying liquid beneath the rear part of a liquid repellent selective membrane by using fuel vapour permeating through it. This induced a surface tension gradient over the carrying liquid underneath the front and the rear parts of the membrane and drove it forward. As the membrane moved and the interface of the carrying liquid was exposed to the ambient air, the fuel was released from the carrying liquid by evaporation (Fig. 1). Thus,

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† Electronic supplementary information (ESI) available: Experimental methods and two videos of locomotion on water (Video S1) and locomotion on oil (Video S2). See DOI: 10.1039/c2sc20355c

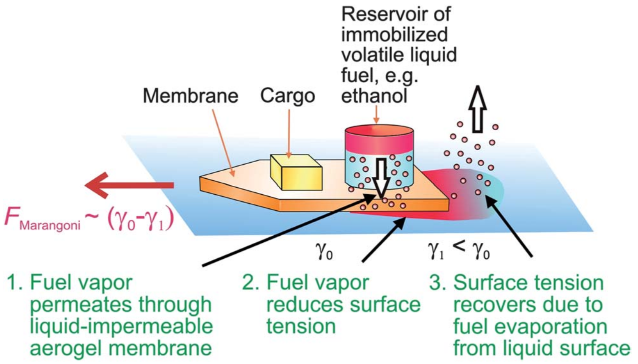

Fig. 1 Self-propulsion of a membrane driven by fuel vapour.

the surface tension of the carrying liquid was restored. For this mechanism to work, the floating membrane must be selective, in the sense that it allows the transport of vapour through its pores, but not of a liquid in order not to compromise floatation.[21] As will be shown below, this new type of Marangoni propulsion enables a steady velocity for a prolonged time owing to the constant supply of fuel vapour through the membrane.

A prerequisite to moving on the surface of a liquid is the ability to float on it. Within the present study, the moving objects were centimetre-scale, fluorinated, nanofibrillar aerogel membranes that are superhydrophobic and superoleophobic and are capable of floating on water as well as on oil.[20] They are composed of 10–20 nm native nanocellulose fibres cleaved from the self-assembled hierarchy of macroscopic cellulose fibres.[22] Nanocellulose fibres have become highly topical as they are proposed to show extraordinary mechanical properties due to their parallel and grossly hydrogen bonded polysaccharide chains.[23] The nanocellulose fibres form aqueous hydrogels, and a subsequent freeze-drying leads to highly porous aerogels.[24] Such mechanically robust aerogels are fluorinated using trichlorosilanes by chemical vapour deposition (CVD), leading to superhydrophobicity and superoleophobicity.[20,25]

As is shown in Fig. 1, a plastic fuel reservoir was put on the rear side of the membrane. It was open at the bottom only, and contained a paper tissue that immobilized a few drops of ethanol as a volatile liquid fuel. The object with its fuel reservoir was then placed on water, where spontaneous motility started due to the Marangoni effect (Fig. 2 and Video S1†). The ethanol evaporated through the aerogel membrane, and as the cup was positioned at the rear of the object, the surface tension of the water (σ_{water}) behind the object decreased due to the formation of a water–ethanol mixture near the water surface (at 20 °C $\sigma_{\text{water}} = 72.8$ mN m^{-1}, $\sigma_{\text{ethanol}} = 22.1$ mN m^{-1}). The gradient of surface tension between the back of the object and its front drove the locomotion. Once the object moved, the ethanol at the water surface evaporated and the surface tension of pure water was gradually restored. The locomotion was at nearly constant speed, even in circular trajectories, indicating that the driving force (surface tension gradient) remained constant. Typically the object was moving for a time scale that is orders of magnitude longer than had been achieved for previously known Marangoni propulsion using liquid fuels.[14,15] In contrast to Marangoni propulsion using camphor as a solid fuel,[16] which requires a channel to confine the motion in a circular trajectory, and which consumes a relatively large amount of camphor, our vapour-driven boat runs on commonplace non-toxic fuels (*e.g.* ethanol), can move regularly at the free liquid surface, and is fuel-economic and simple in design. Thus, a novel type of continuous vapour-driven Marangoni locomotion is presented. In a typical experiment, evaporation of as little as 25 μl of ethanol allowed autonomous motion at a range of 74 m during nearly one hour for a centimetre-sized object. The object was designed to perform a circular trajectory by preparing the proper geometry, which allowed monitoring of the time of each periodic loop. Fig. 2 shows that the locomotion on water took place at an approximately constant velocity of >2 cm s^{-1} throughout the whole experiment of 54 min.

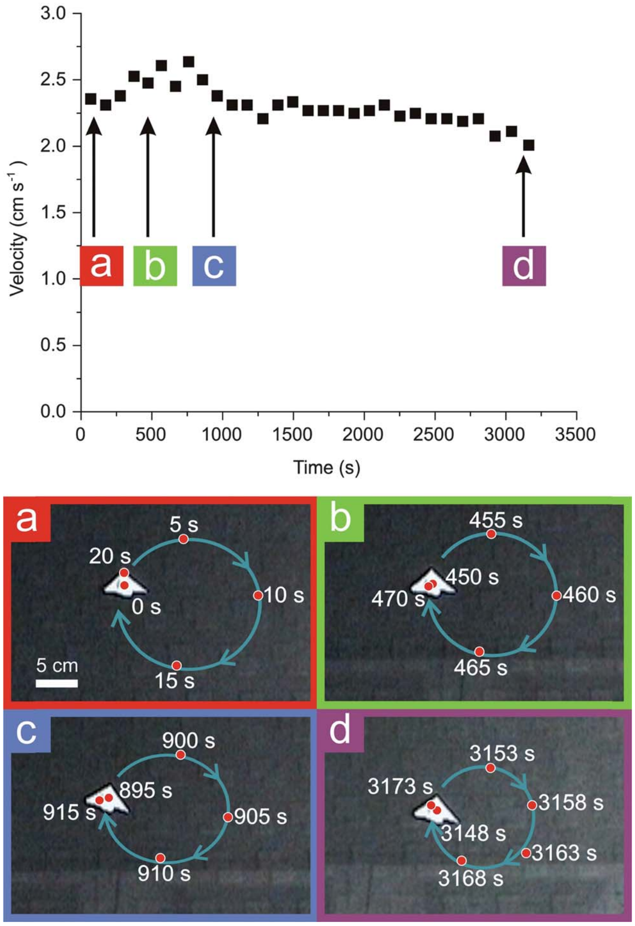

Fig. 2 Steady-velocity locomotion on water based on nanostructured superhydrophobic and superoleophobic aerogel membranes with on-board ethanol as fuel. The vessel is designed to travel in circular trajectories at the free water surface to allow facile monitoring of the velocity. The graph shows the velocity as a function of time. Each data point corresponds to the average velocity for travelling five circular trajectories. Snapshots of the video show the trajectories of the aerogel vessel (time intervals 0–20 s, 450–470 s, 895–915 s and 3148–3173 s). The red spots in a–d are the positions of the vessel. The complete video is available in the ESI (Video S1†).

Tunability of the velocity was demonstrated by changing the type of fuel (see Fig. 3). We selected a series of alcohols with

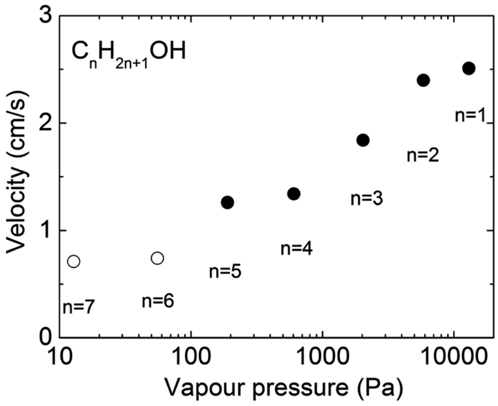

Fig. 3 Tuning the velocity of aerogel locomotion on water with fuel vapours of linear alcohols with different vapour pressures (from methanol to *n*-heptanol). The vapour pressures at 20 °C are determined from the Antoine equation using parameters obtained from NIST Chemistry WebBook (empty circles are approximated values of vapour pressure, calculated by extrapolating the Antoine equation beyond the temperature range of its applicability).

increasing chain length, ranging from methanol to *n*-heptanol, and we observed that the velocity of the aerogel vessel decreases accordingly. The decrease in velocity can be rationalized by the decreased vapour pressure leading to fewer alcohol molecules that modify the water surface and a corresponding lower surface tension gradient.

Next, it was demonstrated that vapour-driven Marangoni propulsion worked also for objects travelling on oil, where pentane was used as the volatile fuel (at 20 °C $\sigma_{\text{paraffin oil}} = 32.9$ mN m^{-1}, $\sigma_{\text{pentane}} = 15.8$ mN m^{-1}), see Fig. 4 and Video S2 in the ESI.† Although the surface tension gradient (and consequently the driving force) is significantly less than for the water–ethanol system, it shows that this vapour-based Marangoni propulsion concept is general.

The fuel carried on board the boat leads to prolonged self-propulsion or autonomous propulsion, and has significant advantages compared to other propulsion systems. In contrast to catalytic propulsion systems requiring floatation on a special fuel-containing solution (*e.g.* Pt-decorated boats floating on aqueous H_2O_2 solution),[3,5,9] the present motility concept is more general as it is valid also on pure water and oil because the object carries its own fuel. Water-walking robots with an on-board energy source have been demonstrated that float by surface tension forces and are propelled by rowing motions of their superhydrophobic metal legs as inspired by the water strider,[26,27] though prolonged autonomous motility was not demonstrated.

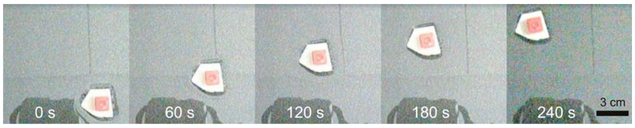

Fig. 4 Video snapshots of the aerogel vessel locomoting on paraffin oil using pentane vapour as the propelling agent. The video is available in the ESI (Video S2†).

Conclusions

In summary, we propose a novel self-propulsion mechanism for floating membranes based on a vapour-induced Marangoni effect. Superhydrophobic and superoleophobic nanocellulose aerogel membranes are permeable to gases but impermeable to oil and water and allow locomotion and floatation on oil and water. The membrane selectivity allows the transducing of chemical energy into steady locomotion, driven by a novel Marangoni effect based on diffusion of a volatile fuel, such as ethanol and pentane, through the membrane. The same behaviour can be expected from other porous membranes that float on the liquid. The locomotion is at nearly constant speed, even in circular trajectories, because the surface tension gradient across the boat is maintained by the following two factors: the fuel supply at a low but constant rate and the restoration of the surface tension by evaporation of the fuel. The velocity of locomotion can be easily adjusted by selecting fuels with different vapour pressure. We expect that membrane-based energy transduction can be generalized also for other dissipative processes. This concept opens new schemes for autonomous soft machines.

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