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Perspective

Using mesoporous thin films as nano-micro-fluidic tools

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Abstract:
Achieving active control on small amounts of liquids represents a substantial challenge in both scientific and engineering aspects. Imbibition of fluids in bodies with nanoscale dimensions enables the spontaneous propelling of nano-flows because of the powerful capillarity at small-length scales. Peculiarities of nanopore imbibition at the thin film level lead to distinctive capillary transport phenomena of fluids across the nanopore matrix. This particular imbibition also impacts on the behavior of the in-contact liquid micro-volumes. These both features add versatile alternatives to the high interest in the management of femtolitre to microlitres amounts of liquids. Herein, we show a brief discussion-outlook based on recent advances in the design of versatile tools to attain programmable nano/microfluidics using mesoporous thin film platforms.

1. Introduction

Taking as a source of inspiration the ubiquity and relevance of imbibition of fluids in porous structures in nature, the underlying physical processes are also becoming highly prominent in nanotechnological fields. The appeal of nanoscale imbibition to nanotechnologists is three-fold: first, it is a spontaneous process; second, its capability to achieve efficient fluid and mass transport; and third, this ability to transport a large number of fluids could be exploited in a wide range of industrial processes. The driving force of the imbibition of liquids in nanopore structures is the capillary action in which the propelled flow usually follows the Lucas-Washburn (L-W) equation, which predicts a square-root of time imbibition kinetics (Xue et al., 2014; Shen et al., 2020; Zeng et al., 2020). One current challenge in the area of nanomaterials imbibition is the design of versatile tools to attain programmable flows beyond the classic L-W dynamic. A distinctive feature of imbibition at the nanopore thin film level is that it is strongly influenced by evaporation, and hence, the imbibition dynamics is different to that usually found on conventional nanopore matrices (Ceratti et al., 2015; Berli et al., 2017; Mercuri et al., 2017b; Khalil et al., 2020). In the case of imbibition in mesoporous thin films (i.e., nanoscale thickness coatings with pores of nanoscopic dimensions (Innocenzi, 2022) (Fig. 1(a) shows a typical example of a mesoporous thin film architecture), since capillary filling and liquid evaporation from the nanopores reach a balance, the capillary infiltration is arrested at a given steady distance (see Fig. 1(b)) (Ceratti et al., 2015; Mercuri et al., 2017b). This arrest of the infiltration is indeed not generally found in the conventional nanoporous structures, where evaporation has a negligible effect and capillary filling expands indefinitely through the nanopore network (Cai et al., 2021). A simple model that combines L-W infiltration and surface evaporation appropriately describes the filling dynamics in mesoporous thin film were the time-dependent (t) of the advancing fluid front position (P) is predicted by Eq. (1) which accounts for the counter-balance between the capillary infiltration (characterized by the coefficient c) and the liquid evaporation rate to the ambient atmosphere (characterized by the time τ) (Mercuri et al., 2017b):

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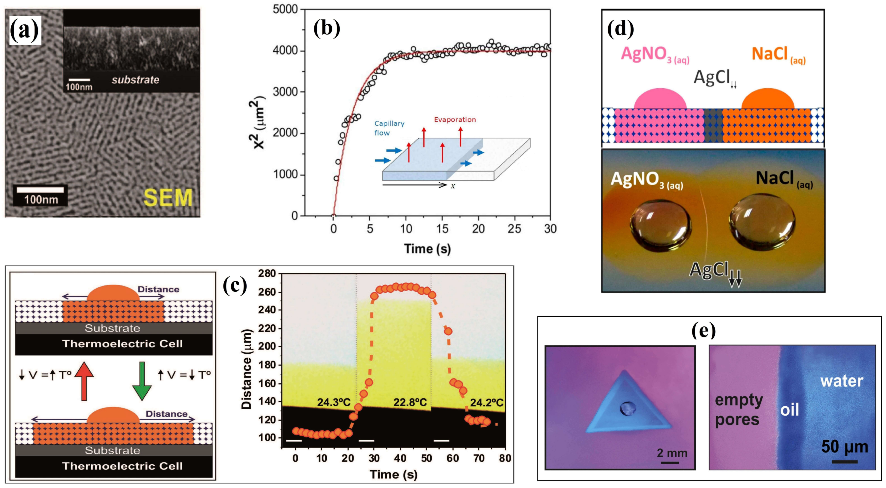

Fig. 1. Capillary imbibition in mesoporous thin film as functional nanoflows. (a) Top-view scanning electron microscope image that shows the nanopores in a typical mesoporous thin film. The inset shows a profile cut of the sample (reproduced with permission from Mercuri et al. (2017a)). (b) Typical squared position of the infiltration front as a function of time on a mesoporous thin film, where an arrested capillary infiltration dynamics is observed. Symbols represent the experimental data and the line is the prediction from the kinematic infiltration-evaporation equation. The inset shows a schematic illustration of transport processes considered in modeling (reproduced with permission from Mercuri et al. (2017b)). (c) Schematic illustration of the experimental setup for manipulating fluids into mesoporous thin films by controlling substrate temperature with a Peltier cell (left) Displacement of the imbibition front from its initial position as function of time (right). Inset: Optical images illustrate the moving fluid across the mesoporous film by thermoelectric actuation (reproduced with permission from Mercuri et al. (2017a)). (d) Optical micrograph of two sessile droplets of $AgNO_3$ (left) and NaCl (right) on a mesoporous thin film showing the characteristic AgCl white line arising from localized reaction when the nanopore-mediated connection is established. The top schematics illustrate the precise capillary-driven delivery of reactants through the film for afterward mixing at the meeting line (reproduced with permission from Mercuri et al. (2017c)). (e) Picture of a millimeter-size two-dimensional (2D) vesicle of predefined shape (left) and a blow-up (right) that illustrate the regions of filled pores with water, oil (barrier) and empty. The immiscible held-localized by capillarity oil prevents the advance of water across the nanopores beyond the barrier (reproduced with permission from Gimenez et al. (2019)).

$$P(t) = \sqrt{c\tau}\sqrt{1-\exp\frac{-2t}{\tau}} \tag{1}$$

Mesoporous thin films are well-known as substrates for microelectronics (i.e., insulators and sensors), advanced optics (i.e., photovoltaics and photonics), as well as for high area nanomaterials in catalysis or selective membranes (Sanchez et al., 2008; Innocenzi et al., 2013). Notably, these versatile nano-architectures also offer unique opportunities for many nano to micro fluidic applications.

2. Handling into-nanopores liquids (nanoflows)

Taking advantage of their particular fluid-nanopore interplay, mesoporous thin films were recently employed as robust platforms for achieving control over the imbibition dynamics. The fluid imbibitions in mesoporous thin films are not merely flows through the pore space; they are indeed functional nanoflows. This platform also offers a convenient tool for studies of fluid-nanopores interplay whereas other techniques are arduous. The process of nanopore imbibition can be visualized under an optical microscope thanks to the thin-film interference of reflected light, where the liquid-filled pore region produces a refractive index contrast in relation to the empty pore space (Mercuri et al., 2017b; Vincent et al., 2017). Tuning the balance between capillary infiltration and liquid evaporation via thermal inputs allows a controlled transportation of fluids across the nanopores, thereby modulating the advancement of liquid into the porous matrix (see Fig. 1(c)) (Mercuri et al., 2017a). It is worth mentioning that small changes in temperature have a pronounced impact on the fluid displacements, which in turn determines the versatility of the methodology. This strategy was further used to switch a nanofluidic connection between droplet-landmarks by means of voltage control using a Peltier cell (Mercuri et al., 2017a). On the other hand, a photoactive gating of capillary infiltration into mesoporous thin film was attained by carefully pore surface functionalization to induce a wetting transition triggered by luminic stimuli (Khalil et al., 2021). The fluid-nanopore interplay also allows emerging platforms capable of performing nanoparticle precipitation zones at desired locations into the pore space, through even an intrinsic banding pattern fashion (see Fig. 1(d)) (Mercuri et al., 2017c). This controlled chemistry is not primarily limited to precipitation reactions. Rather, the incentive for this work comes from the desire to create nanoflow-controlled chemical regions. These earlier attempts to perform specific reactions over localized regions have mainly focused on free flows across the nanoporous network. A hybrid platform integrating

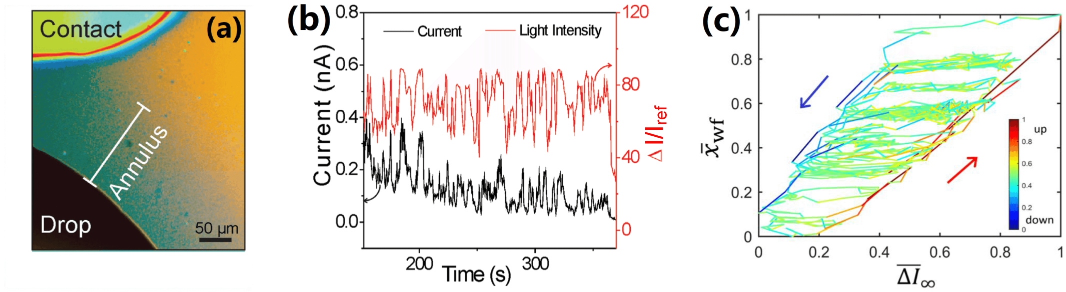

Fig. 2. Coupled capillary imbibition-evaporation-condensation phenomena lead to oscillatory effects. (a) Optical microscope image showing the space between the electric contact and a water droplet deposited on the mesoporous film; the spontaneous oscillations of the infiltrated annular region are converted into tiny amounts of electric energy (reproduced with permission from Gimenez et al. (2018)). (b) Electric current (black curve) measured during the water front oscillations; the reflected light intensity (red curve) measures the instantaneous oscillating water content in the film, which perfectly correlates to the generated electrical current (reproduced with permission from Gimenez et al. (2018)). (c) Wetting-front position as a function of the light intensity measured far from the drop, which accounts for the vapor concentration in the environment of the mesoporous film; the red and blue paths indicate forward and backward movements, respectively, while the green zones represent pseudo-steady positions. The curves are reminiscent of adsorption-desorption isotherms of the mesoporous films; furthermore, the hysteresis loop of such isotherms is at the origin of the cycling behavior of the wetting-front (reproduced with permission from Urteaga et al. (2019)).

paper-based microfluidics and mesoporous films was also able to mold capillary imbibition and chemical reaction shapes with extra features such as the capability to achieve gradients and size selectivity (Mercuri el al., 2018).

As an important contribution to the nanofluidic control into the mesoporous thin films platforms, the recently reported fluid-fluid self-supported vesicles of two-dimensional arbitrary shapes composed of oil printed pore-perimeters into mesoporous thin films has a similarity to biological barriers in the compartmentalization of the cell (see Fig. 1(e)) (Gimenez et al., 2019). The oil strongly contains and partitions the aqueous domains that maintain their structure due to capillary jamming. This work also showed that these aqueous fluidic 2D domains can communicate via nanopore capillarity in ambient conditions where each compartment is responsible for one area in space and allow conducting specific reactions over predefined regions with accuracy.

In the case of films with mesoporous worm-like morphologies, another remarkable phenomenon was found: the nanopore imbibition displays a spontaneous oscillatory movement instead of reaching a steady-state position (Urteaga et al., 2019). Further, these oscillations can be converted into small electrical currents by using electrodes integrated to the mesoporous platform (See Figs. 2(a) and 2(b)) (Gimenez et al., 2018). The origin of this oscillatory imbibition behavior can be traced back to condensation-evaporation imbalances, which in turn follow spontaneous variations of the vapor pressure due to air advection stream in an open environment. Furthermore, a calculation indicates that the observed wetting-front oscillations are intrinsically related to the particular hysteretic character of the adsorption-desorption isotherms of these mesoporous nanostructures (see Fig. 2(c)) (Urteaga et al., 2019). These self-oscillating flows generated provide one more prospect of conceiving novel scenarios to design new nanoflow operations.

3. Manipulating in-contact liquids (microflows)

In a separate but related thread, the ability to manipulate the dynamic of liquids on surfaces is of vital importance for a variety of relevant applications, ranging from thermal management technologies to microfluidic handling. In this context, the particular capillary imbibition of fluids across a nanopore thin film network was thus exploited to control restricted/discrete in-contact liquid volumes. In a recent work, a substantial enhancement of liquid evaporation rate was observed when droplets are on mesoporous thin film surfaces related to the key role of the arrested capillary imbibition in the drop periphery (See Fig. 3(a)) (Gimenez et al., 2020). This work also revealed that this nanopore-catalyzed evaporation leads to counter-intuitive phenomena: cooler or more saline droplets evaporate faster. These unusual features provide routes to accurately controllable liquid dynamics aimed at micro-mixing tools and vapor dosing. More recently, the peculiar transport of fluids across a mesoporous thin film was also exploited to achieve that a pair of chemically complementary droplets can spontaneously evolve to a chemospecific stimulus-response operation, which is a resemblance of an emergent “intelligent” behavior (see Fig. 3(b)) (Pizarro et al., 2022). The spatially separated droplets interact and subsequently act by themselves via underlying capillary-driven chemical messages that disrupt the energy landscape, leading to a macroscopic response. The autonomous non-reciprocal interactions triggered lead to the generation of distinctive droplet dynamics with shape transformation and complex behaviors reminiscent of basic immune system cell actions such as pseudopod emission and phagocytic-like functions (See Fig. 3(c)). The inter-droplet communication propelled by nanopore capillarity and associated chemical activity (catalytic decomposition of hydrogen peroxide) are the primary physical ingredients behind the surprising observed behavior (Pizarro et al., 2022). The

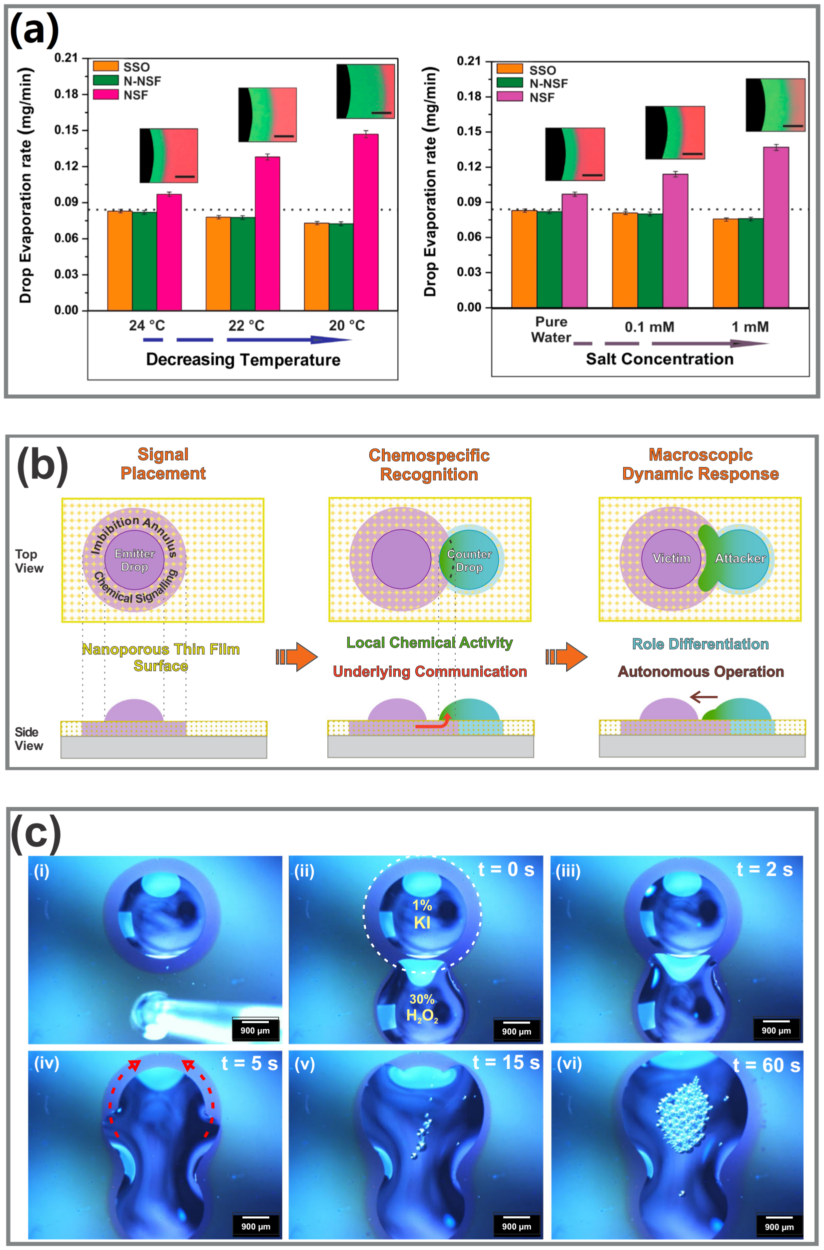

Fig. 3. Capillary imbibition in mesoporous thin films impact on in-contact liquid behaviors. (a) Evaporation time measurements for drops placed on the nanoporous and non-nanoporous silica thin films, and the silicon substrate only. The mesoporous layer has a significant effect on the drop evaporation time. Note that nanopore-supported droplets evaporate faster when they cool or salt concentration increases. Both dependencies are opposite to the typical behaviors as indeed it is shown for the flat substrates. The inset images illustrate that the phenomena are associated with the arrested capillary imbibition region around the droplet that controls the overall evaporation process. The imbibition region can be clearly seen due to the thin-film interference of reflected light, where the liquid-filled pore region at the vicinity of the drop produces a refractive index contrast in relation to the empty pore space (reproduced with permission from Gimenez et al. (2020)). (b) Schematic concept of the capillary-driven nanopore communication to attain complex inter-droplet responses. Droplets act as emitters of nanopore-mediated chemical messages and thus can be noticed by a spatially separated counter-droplet. In turn, chemically complementary droplets can evolve to become locally active with transductional chemo-mechanical behaviors in response to the capillary-driven cues from the emitting droplet (reproduced with permission from Pizarro et al. (2022)). (c) Sequenced images to show a H_2O_2 droplet engulfing a spatially separated KI droplet on a nanoporous thin film surface. The H_2O_2 droplet extends phagocytic-like arms in response to interaction with the capillary-driven fluid released across the nanopores from the KI droplet (reproduced with permission from Pizarro et al. (2022)).

strategy provides a transformative approach for controlling the attraction and coupling of droplets on surfaces, which will have a central impact on modern microengineering and biomedical applications.

4. Conclusions

In short, some of the most interesting developments in nanofluidic concern the exploitation of spontaneous fluid transport processes since, in many cases, their features exceed the capabilities of present day man-made methods. In this sense, the particular interplay between liquids and mesoporous thin films could lead to simple routes to develop novel tools for precise handling of fluids at different scales (from nano to microflows) in applications ranging from diagnostic assays to the production of high-value (bio) chemicals. It will be interesting then to learn more about the role of capillary infiltration-evaporation balance in directing the into-pores or in-contact liquids. Finally, it will also be exciting to explore the use of photonic based mesoporous structures (Hidalgo et al., 2011; Gazoni et al., 2017), which would launch the emergence of a diversity of synergic optofluidic effects for advanced applications.

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Conflict of interest

The authors declare no competing interest.

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