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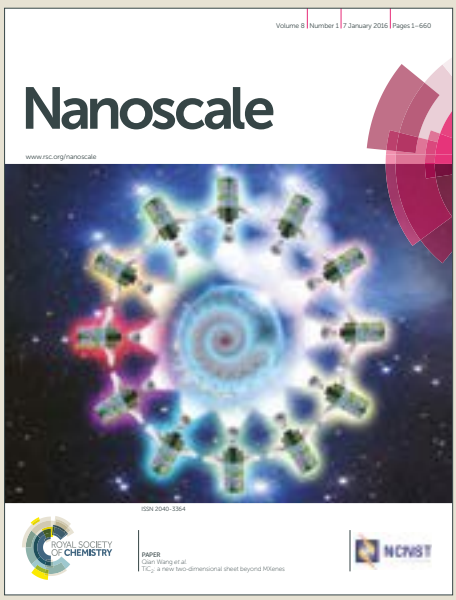

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COMMUNICATION

Electrical-Current Nanogeneration Driven by Spontaneous NanoFluidic Oscillations

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R. Gimenez,[a] M. Mercuri,[a] C. L. A. Berli*[b] and M. G. Bellino*[a]

Exploiting natural phenomena is a central route for providing electricity to sustainably drive wearable electronics. Here we report a nano-scale water-driven energy generator that produces tiny electrical currents from spontaneous wetting-drying oscillations in mesoporous thin films. The system was fabricated with a wormlike mesoporous silica film, which was packed in between Cu and silicon contacts. The nanogenerator runs autonomously when a water droplet is laid over the film close to the Cu electrode, as water infiltration into the film under the electrode produces a direct-current. Wetting-drying cycles, which are spontaneously triggered by water evaporation, are perfectly correlated to the generated electrical current. The autonomous water displacement through the film yields a sustained energy conversion until the droplet reservoir vanishes. This novel water-driven nanogenerator opens new alternatives for versatile, mobile and cost-effective self-powering of nanosystems and nanodevices.

A self-oscillating system is an attractive proposition for harvesting energy. If accomplished on the nanoscale, such power sources could operate nanodevices fabricated with nanostructures (such as nanotubes, nanowires, and graphene),[1-4] which usually require very low power. Nanofluidics has proved to be a very useful and exciting platform for nanodevices.[5-8] In this sense, the highly controlled confined spaces of mesoporous materials offer opportunities for the exploitation of nanoscopic flow.[9-11] When a sessile drop is deposited over a mesoporous film, it exhibits an annular region of the wetted material formed by the arrested capillary infiltration.[9] The dynamics of the liquid-vapour interface are governed by the competition between capillary filling and film surface evaporation, thus the advancement of fluid front into the porous matrix is halted at a defined position, for a given temperature.[12] Furthermore, in the case of mesoporous films with wormlike nanostructure, a remarkable phenomenon has been observed: the fluid front displays a spontaneous oscillatory movement instead of maintaining a steady position.[9] We demonstrate here an approach to convert the nanofluidic energy from these spontaneous oscillations into electricity. The nano-current generated by this autonomous water displacement through the film has the potential of harvesting energy for the operation of optoelectronic devices,[13] biosensors,[14] resonators,[15] and more.

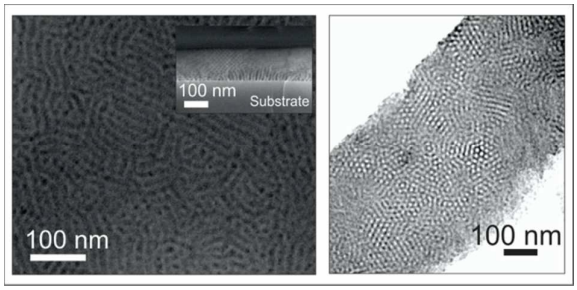

Fig. 1 Structural characterization of the mesoporous sample. SEM (left) and TEM (right) micrographs; the inset in the SEM image shows a profile cut.

Our study is then based on a 100 nm thick wormlike mesoporous silica film (see Figure 1), grown on a p-type silicon substrate, using F-127 as a surfactant template,[9] by combining sol–gel chemistry and evaporation-induced self-assembly (see Supplementary Information for experimental details).[16,17] A top copper electrode (200 nm thick and 1 mm in diameter) was deposited above the mesoporous thin films and contacted by a probe station under an optical microscope to achieve precise positioning. The experimental setup is schematically shown in Fig. 2a defined by two contacts (Si and Cu) separated by a supramolecularly template mesoporous oxide film. The output current between the Cu/Si contacts when a sessile drop of liquid (1 µl) is deposited 120 µm beside the metal contact onto the mesoporous film (see Fig. 2b), was measured by an external circuit at room temperature and no external voltage was applied at any stage of the experiment. Placing the drop

[a] *Comisión Nacional de Energía Atómica, CONICET, Departamento de Micro y Nanotecnología, Av.Gral. Paz 1499, 1650, Argentina.*
E-mail: mbellino@cnea.gov.ar
[b] *INTEC (Universidad Nacional del Litoral-CONICET) Predio CCT CONICET Santa Fe, RN 168, 3000 Santa Fe, Argentina.*
E-mail: cberli@santafe-conicet.gov.ar
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leads to a significant current generation between the two electrodes according to spontaneous wetting of the mesoporous matrix under the Cu electrode area. Both the generated current as a function of time and the corresponding evolution of the annular wetted region were recorded simultaneously.

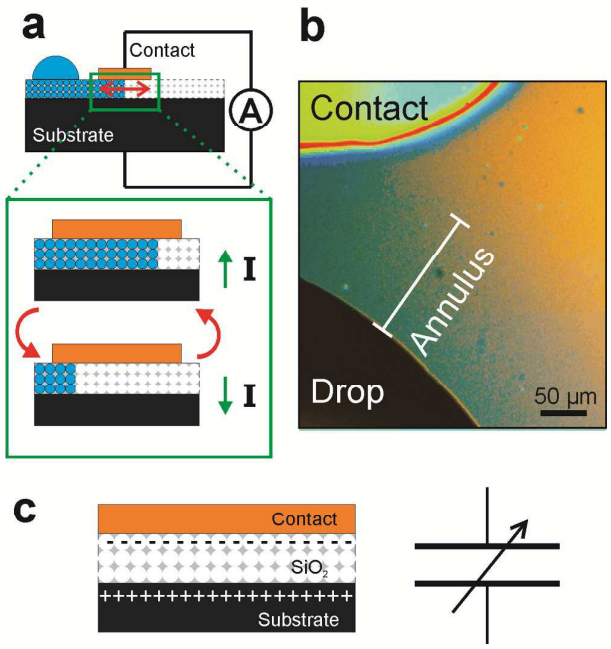

Fig. 2 Mechanism of the nano-current generation driven by a spontaneous nanofluidic oscillation. (A) Schematic illustration of the setup for measuring the output current and the nanofluidic configurations. (B) Typical top-view microscope image of the contact and water droplet deposited on the mesoporous film showing the infiltrated annular region. (C) Sketch representation of the mesoporous metal-oxide-semiconductor system (left panel) and corresponding electrical model (right panel): the water uptake and release processes modify the effective dielectric permittivity of the film, hence the system may act as a variable capacitor.

A temporal location of current peaks is directly registered at the time of the maximum levels in the capillary water infiltration. The wetted region can be clearly seen because it produces a refractive index contrast in relation to the outer dry zone. This remarkable phenomenon can be vividly observed in the real-time videos taken during experiments. Movie S1 (Supplementary Information) depicts the correlation between the current peaks and the spontaneous filling and emptying oscillations accelerated by a factor 2. A circuit current is generated and shortly rises up to 0.65 nA when the fluid front reaches its maximum distance under the Cu sheet in about 2 s after depositing the drop (Fig. 3a). The later fluctuations in the measured current can be explained by the oscillatory behaviour of the liquid–vapor interface. A jump was successively observed when the displacement of the fluid front was forward, and the current immediately fell back once the fluid front goes back (Fig. 3b), and the current immediately fell back to the baseline once the droplet completely evaporated. Moreover, Fig 3c shows a tight correlation between the time-dependent light intensity reflected from the wet film and the generated electrical current. Each intensity jump (thought to be proportional to the instantaneous film water uptake) causes a tiny pulse of electricity. The current sequence displays an oscillatory behaviour with a period around 10 s, as shown in the inset of Fig 3a, in accord with light intensity near the electrode (Fig. 3c). The progressive decrease in sharp output peaks is due to the fact that water supply from the sessile drops progressively diminishes as the droplet evaporates; this effect is evident in Movie S1 (Supplementary Information), where the reflected light from the droplet surface gradually changes until complete evaporation. These results together demonstrate that a current nanogenerator with the use of oscillating nanofluidic in mesoporous films can be performed, even if the procedure has not been yet fully optimized.

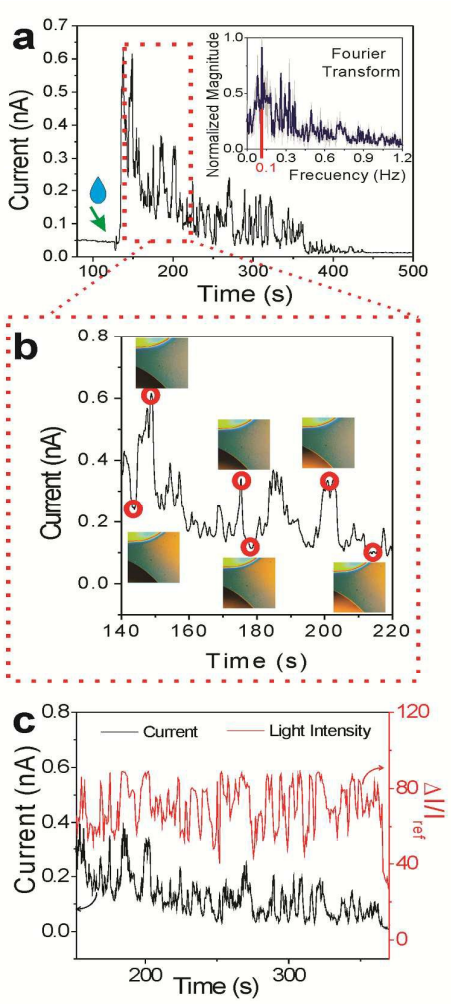

Fig. 3 Output of the nanogenerator. (A) Current measured when the water drop is deposited on the film; the associated Fourier transform is given in inset. (B) Zoom of the current evolution, where the inset pictures illustrate the correlation between the annulus width and current maxima/minima values (red circles), at the respective times. (C) Reflected light intensity, as a measure of the instantaneous water content in the film, perfectly correlates to the generated electrical current; the calculation of light intensity from image analysis is described in the Supplementary Information.

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Actually, the generated output power was estimated to be 1 nW in the current experimental design, taking into account the output current and the electrical resistance of the device along the current direction (on the order of 10^9 Ω). To have a reference, the power used to operate a single nanowire/nanotube based-device is about 5-10 nW;[1-4] thus an enhanced system based on this work might be a candidate to operate such nanodevices.

Let us now discuss the underlying mechanism of the current generation. At first glance, it may be natural to attribute the driving force to electrokinetic phenomena, as in streaming currents[18,19] or ion-enrichment/depletion effects,[20,21] where the relative movement of fluids through charged porous media contributes to current generation. However, upon replacing the Milli-Q water by different concentrations of an ionic solution (NaCl concentrations from 0.1 mM to 0.1 M), the observed currents remain practically unchanged in respect to the measurements performed with Milli-Q water alone (See Fig 4). This finding relativizes out electrokinetic phenomena as potential sources of the observed currents, taking into account that the thickness of the electrical double layer inside the pores decreases with ionic concentration, which substantially diminishes electrical effects under flow. In contrast, the generated current in Fig 4 stays the same even if a high ionic strength solution is applied. Furthermore, an interesting manifestation of varying ionic concentrations is that the output current can reliably be maintained during the whole test until droplet-reservoir evaporation. This may be because salt decreases water evaporation, hence larger annulus widths are attained for higher NaCl concentration,[10] which favours a more sustained water supply to the film under the electrode.

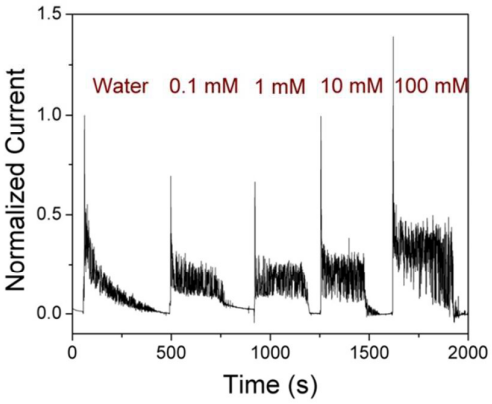

Fig. 4 The response of the nanogenerator to different levels of NaCl in the working fluid. The tallest spikes mark the onset of drops deposition, with increasing salt concentrations from left to right. Normalization was done by using the maximum current in pure water.

In this context of results, the driving mechanism for creating the current discharge may be attributed to the variation of dielectric properties of the mesoporous layer packed between the copper and silicon contacts. Water uptake changes the effective dielectric constant of the mesoporous film since it is a composite material layer made by the macroscopic mixture of 3 homogeneous components (air, liquid and oxide), and the capacitance of the system is very sensitive to wetting-drying cycles.[22] As nanofluidic oscillations keep varying the dielectric constant of the mesoporous metal-oxide-semiconductor (MOS) capacitor, the reorganization of charges between the electrode and the Si substrate would produce the electrical current sensed through the ammeter. Thus, the system could act as an electrostatic harvester,[23] which is essentially a variable capacitor, as shown schematically in Fig. 2c. When subjected to external vibrations, the capacitance of the harvester can be changed cyclically by either changing the effective area or the distance between parallel plates. In the case reported here, the variation of capacitance occurred by changes in the effective dielectric constant, without any contact displacement. To further explore this hypothesis, we have independently measured the meso-MOS capacitance when a drop of water was deposited onto surface, and found a substantial capacitance variation in the same time lapse (see Fig. S2 in SI). The change observed is sufficient to explain the amount of charge transferred during current generation experiments (for example, 36 nC in the case of Fig 3a, calculated as the time integral of the electric current curve). The capacitance curve (Fig. S2 in SI) also exhibits small fluctuations during growth, which are directly related to wetting-drying cycles. It is interesting to observe that, although the output current also fluctuates, it is not alternating but always positive. The reason for this could be associated to a large time response of the system during drying intervals, so that the negative part of the current curve cannot be reached, and the overall result is a fluctuating direct current. Of course, this mechanism of electrostatic generation requires a polarization or initial charge in the capacitor, which is normally solved by introducing an electret.[23] Here the mesoporous silica film could naturally act as such element[24,25] by creating the initial differential charge, positive for the p-type Si and negative for the mesoporous film, as drawn in Fig. 2c.

It is appropriate to point out that additional tests were carried out to get more insights on this current generation phenomena. The experimental design has been tested by using different silica films. Using the design shown in Fig. 2A, simply replacing the wormlike porous array with an array of ordered nanopores (See Fig. S3 in SI), slight currents were observed when a water droplet was laid over the film close to the Cu electrode (See Fig. S4 in SI). In this case, smaller imbibition distances in comparison with the worm-like films are produced and the film wetting does not display an oscillatory behaviour.[9] The tiny current signal that arise in this ordered mesoporous system may be attributed to little alterations of wetting into the nanopores due to the humid environment around the drop. In addition, no activity was detected when the mesoporous layer was replaced with a non-porous silica film (see Fig. S4 in SI), which indicates that the wetting-drying process of the mesoporous material under the electrode is essential. In addition, as mentioned above, the oscillation-induced electricity is also recorded when using gold as electrode material (Fig. S5 in SI), which again suggests that the effect is inherent to the wetting-induced change of the meso-MOS capacitance.

Finally, it is worth mentioning that electrostatic harvesters have been before demonstrated in vibration-based devices but not in a wetting-drying nanofluidic system. Nevertheless, the principle of dielectric variation has been proved in a microfluidic device designed to handle a transit of bubbles

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between the capacitor plates.[26] Further research is required to fully discern the basic origin of the generated electric current, taking in mind that a concurrence of physico-chemical phenomena could also be contributing in such a complex system. Nevertheless, even if the working principle is still open to discussion, the aim of this communication is to show the possibility to harvest energy from a subtle natural phenomenon that takes place on mesoporous films.

Conclusion

In summary, we have shown that nanofluidic oscillations from capillary infiltration in mesoporous films can generate a sustained current. In comparison with the previously reported methods to harvest electricity from nanosystems, produced externally by, for example, vibrations[27] or (bio)chemical reactions,[28,29] the electricity generation here is obtained through a spontaneous process without mechanical work or chemistry energy input. Essentially, part of the energy associated to spontaneous water condensation in mesoporous films is converted into electricity. The integration of the nanofluidic phenomena in the mature MOS technology that is related to most planar devices and integrated circuits increases significantly its technological applications. This novel methodology is fully compatible with the techniques and substrates used in the sensor, microfluidic and microelectronics industry, opening a path to a new nanotechnology that harvests electricity for a variety in nanodevices and portable electronics fuelled only by water.

Conflicts of interest

There are no conflicts to declare.

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Table of Contents.

Here we describe how spontaneous nanofluidic oscillations from capillary infiltration in mesoporous films can be converted into small electrical currents.