Unidirectional water pumping in zeta-potential modulated Nafion nanostructures

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Article

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Abstract

We report on a new and versatile self-driven polymer micropump fueled by salt which can trigger both radial recirculating and unidirectional fluid flows. The micropump is based on the ion-exchanger Nafion, which produces chemical gradients with the consequent local generation of electric fields capable to trigger interfacial electro-osmotic flows. By combining new nanofabrication strategies for Nafion structuring in microarrays with a fine tune modulation of the surface zeta potentials it was possible to redirect electro-osmotic flows into unidirectional pumping. The experimental data have been contrasted with numerical simulations accomplishing good agreement. Nafion micropumps work in a wide range of salt concentrations covering more than four orders of magnitude, from micromolar to the millimolar range, and can be regenerated for reusability. This novel micro-array of chemically powered Nafion pumps constitutes a very appealing proof of concept for a new generation of wireless micro/nanofluidic networks.

Introduction

Interfacial diffusio-osmotic or/and electro-osmotic fluid flows triggered by self-generated chemical gradients are the basis behind chemically propelled micro/nanomotors or swimmers. The intense activity in this fascinating field in the last years has provided very appealing demonstrations of multitasking swimmers^{1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20}. The immobilized counterparts of micro/nanomotors are micropumps, sharing the same working principle of the swimmers, but driving the flow of the surrounding fluid instead of self-propelling in a fluid at rest²¹. These immobilized versions of motors are also especially suitable for better experimental probing and understanding the phoretic mechanisms behind swimmers²¹. Micropumps are also promising platforms for many applications such as mass release, transport, accumulation, and clearance^{5,22}; material patterning at precise locations^{23,24,25}; or in sensing applications^{22,26}.

Self-powered micropumps of different material composition and working principles have been investigated in recent years. Most studies have focused on catalytic bimetallic or semiconductor/metallic pumps governed by electro-osmotic flows^{5,27,28,29,30,31,21,32,33}. Other type of pumps have combined passive materials with metals, semiconductors, solid salts, polymers or enzymes, switching on ionic, neutral diffusio-osmotic, or density-driven convective flows induced by the gradients of ions or neutral species generated at the active part of the pump^{31,34,35,36,37,38}. Many of these pumps are triggered by the hydrogen peroxide decomposition reaction which can be toxic for some applications, especially in the biological context. Therefore, there is always a need to search for more innocuous chemical fuels or novel reaction mechanisms to overcome such limitations. The use of motors or pumps fed by enzyme substrates is a very elegant way to expand applications in the biomedical field^{9,10,36,37,38}. Another alternative using innocuous fuels are self-powered pumps or swimmers made of ion-exchange polymers. In this context, a pump based on immobilizing particles of ion-exchange resins on glass with the capability of triggering electro-osmotic flows with trace amounts of salts has been reported³⁹. However,

this interesting kind of ion-exchange pump becomes inoperative at concentrations above 80 μM , a fact that could hamper some biomedical and environmental remediation applications which need to operate at higher salt concentration.

Another important feature to achieve with self-powered pumps is fluid flow unidirectionality. The vast majority of studies have focused on just demonstrating fluid pumping through local recirculated flows towards and away from active patches. However, to expand the applications of micropumps in the field of wireless micro/nanofluidics without the use of external fields or pressure sources, achieving unidirectional fluid pumping is essential. As far as we know, only one study has addressed unidirectional water pumping using an array of three-dimensional photochemically active Au/TiO_2 Janus pillars acting as pumping walls.⁴⁰ The pillars catalyze the water splitting reaction under UV illumination, giving rise to local osmotic flows around them. The cooperative effect of the flows generated by an array of pillars leads to unidirectional macroscopic flow for a careful choice of the geometry and arrangement of the pillars. The lack of studies reporting wireless fluid flow unidirectionality might be rooted in the difficulties to match the proper disposition and pumping mechanism to accomplish a constructive effect using an array of pumps. Fluid flow unidirectionality is not simply achieved by a periodic repetition of active structures. Instead, a suitable geometrical layout and a controlled surface nanoengineering of the active materials are needed to sustain fluid flow motion in one direction,

Here, we report on a new self-activated micropump based on Nafion which can pump fluid using salts as chemical fuel and can be nanostructured to achieve unidirectional pumping. We harness the ion-exchange capabilities of Nafion⁴¹ to induce both radial or unidirectional tangential electroosmotic flows in the presence of salts^{42,43,44,45}. To accomplish long-range unidirectional fluid pumping, an array of Nafion microstrips are patterned with novel and highly controllable nanofabrication strategies. These active strips are integrated, in turn, into an array of adjoining strips with different zeta potential (ζ). Thus, the novelty of this wireless pump system lies in the design of an ion-exchange powering system integrated in a nanofabricated array with fine-tuning modulation of zeta potential surrounding the active Nafion to control the direction of the flow. We prove fluid pumping in a wide range of salt concentrations covering more than four orders of magnitude, from micromolar to the millimolar range. We also show that these pumps can be easily regenerated for reusability without almost no loss of performance.

This study also expands the versatility of Nafion material from the well-known application areas of the chlor-alkali industry, fuel cell technology^{41,46,47,48,49} or biosensor technology^{50,51} to the appealing field of wireless micro/nanofluidic networks and self-propelled micro/nanomotors, promoted by the new strategies achieved in Nafion nanopatterning.

Results And Discussion

Nafion pumps driving radial flows

Nafion is a perfluorinated sulfonic acid ionomer with high performance cation-exchanger capabilities apart from other attributes such as very high ionic conductivity, excellent thermal and mechanical stability, biocompatibility and antifouling characteristics⁴¹. We first demonstrate the capability of Nafion to trigger fluid pumping in a simple configuration which activates radial flows. The pump layout consists of a 100 μm diameter and about 600 nm thick Nafion disc surrounded by a region in which Nafion has been mostly deactivated. The fresh Nafion material is in its protonated form and deactivation is achieved by e-beam lithography which scissors Nafion $-\text{SO}_3^-$ moieties decreasing its ion-exchange capabilities⁴⁴.

Figure 1a (top) schematizes a cross section of the micropump under study illustrating the pumping mechanism. Fluid pumping is triggered when the patterned Nafion system is immersed in aqueous salt solutions due to the exchange of protons by the salt cation. The pumping mechanism can work with many different salts, since Nafion can exchange protons by many positive ions. In our case we have chosen LiCl as electrolyte due to the low diffusion coefficient of this cation which improves the pumping performance as will be explained later on.

In the experimental device, the fluid flow is followed by tracking the motion of polystyrene based tracer particles. Figure 1a (bottom) shows the typical motion behavior of the colloidal tracers close (bottom left) and far away from the surface (bottom right), respectively. Particles close to the surface move toward the Nafion disc, however, as they approach the disc edge their trajectory bends upward in the direction perpendicular to the disc and finally bend outwards the disc due to fluid continuity and the presence of the top wall of the cell (See Movie 1 and 2 in the Supplementary Information).

The time evolution of the pump performance was evaluated by tracking the average radial velocities of the polystyrene tracers dispersed in $1 \cdot 10^{-4}$ M of LiCl at the region close to the surface (Fig. 1b). In general, particles increase their radial velocity when approaching to the disc, exhibiting maximum values at 60–80 μm from the disc center. Then the radial velocity decays inside the Nafion region because the particles are pushed up by the fluid or because they are retained on the disc when the speed of the fluid is not large enough to lift them, a phenomenon that is more probable to occur at large times. Maximum tracer velocities of around 30 $\mu\text{m/s}$ have been detected at very short times. These are large values compared to those obtained with other catalytic pumps combining metals in H_2O_2 solutions²⁹ or metals/semiconductors in water^{30,31}. The maximum velocity was decreasing to values around 2 $\mu\text{m/s}$ when reaching half an hour of actuation. The pump was able to continue running for more than 45 minutes, which is remarkable considering that the layer of Nafion is only 600 nm thick.

The mechanism responsible for fluid pumping is illustrated schematically in Fig. 1a and has been verified by the simulations described in the Supplementary Information. As briefly mentioned before, the reason behind the performance of these pumps lies in the Nafion capability to exchange ions. In our study, the starting Nafion sample is the protonated Nafion form. In this case protons are expelled from Nafion to the liquid interfacial region when immersed in a salt containing electrolyte such as LiCl. In exchange, lithium ions are incorporated into the Nafion film and consequently are depleted from the electrolyte. A concentration gradient and an electric field are spontaneously built-up near the interface due to the

unequal diffusion coefficients of the exchanged ions as proved by previous studies^{44,52} and shown by the simulations in the SI (see Fig. S2). Li ions were in fact chosen due to the low diffusion coefficient of this cation, thus providing higher difference of diffusion coefficients with respect to protons, which results in larger electric field generation near the interface. Such electric field is directed towards the Nafion surface when protonated Nafion is immersed in a salt-containing electrolyte (see Fig. S2).

The interplay of the tangential component of the electric field with the surface zeta potential switches on fluid flows whose direction is dictated by the sign of the surface's zeta potential⁵³. We have measured the zeta potential of Nafion and deactivated Nafion from the streaming potential /current of planar surfaces of these materials using $1 \cdot 10^{-4}$ M LiCl as electrolyte and pH of 5.7. The Nafion region is the one with largest negative zeta potential (-73 ± 3 mV). The deactivated Nafion exhibits less negative zeta potential (-37 ± 3 mV) with respect to Nafion which is expected due to the removal of sulfonic groups. Since the zeta potential of the surface (both deactivated Nafion and Nafion) is negative, tangential electro-osmotic and chemi-osmotic fluid flows towards the Nafion disc are switched on with the consequent formation of convection rolls. It is important to clarify that although there is a zeta potential gradient at the boundary between Nafion and deactivated Nafion, this gradient is not responsible for generating the electric field that moves the fluid. The key parameter in switching on the fluid pumping is the tangential component of the electric field generated by the exchange of ions with different diffusion coefficients. Simulations show that this tangential component of the electric field is almost insensitive to the value of the zeta potential of the material surrounding the active Nafion (see Fig. S3). The zeta potential of the surface sets the sign of the charge and distribution of mobile counterions that move in the presence of the tangential electric field, dragging the fluid along. Simulations also confirm that there is no fluid flow in the absence of ion-exchange, and that there is pumping even if the zeta potentials of both surfaces would be the same.

The pump performance has also been evaluated experimentally as a function of different concentrations of LiCl as depicted in Figure S5a. The radial fluid velocity of the tracers exhibits a non-monotonic behavior. It increases with salt concentration at very low concentrations of salts but then starts decreasing at higher concentrations. Previous studies on the self-generated electric field as a function of salt concentration have also shown a similar behavior which was attributed to a change in the rate determining step involved in the ion exchange mechanism, from a diffusion-limited process at very low salt concentration to a process controlled by the ion-exchange reaction at higher salt concentrations⁴⁴. Since the electric field dictates the fluid flow, a similar effect is expected to occur with the radial fluid velocity as a function of salt concentration. Even so, fluid pumping remarkably persists even at mM salt concentrations. Thus, these Nafion pumps are very promising for applications since they can be operative in a wide range of salt concentrations, in contrast with other pumping mechanisms.

A very interesting feature of these pumps is their reusability after a regeneration step of the pump. The fresh Nafion pump is in its protonated form and after use with LiCl electrolytes the pump is loaded with Li^+ ions. The Nafion pump was regenerated to the protonated form by immersion in $1 \cdot 10^{-2}$ M HCl for 6 hours. Then the pump was reused in $1 \cdot 10^{-4}$ M LiCl. Fig. S5 b compares the radial velocity of tracers in

1.10^{-4} M LiCl on a freshly prepared pump with that obtained when using the same pump for a second time after a regeneration step. The pump performance was almost the same, with only a slightly decrease in speed after regeneration.

Nafion pump driving unidirectional flows

The most common strategy to sustain unidirectional fluid pumping over long distances is to repeat periodically the basic structure that generates fluid motion. However, in this case the combination of alternating strips of active and deactivated Nafion would not accomplish unidirectional pumping since multiple convection rolls would be produced at the Nafion strips instead of unidirectional flow. The electric field pointing towards the active Nafion pad together with the symmetric surface zeta potential at both sides would always direct the fluid flow towards the active Nafion patches as illustrated in Fig. 2a. To rectify the fluid motion in one direction it is important to break the surface charge symmetry around Nafion. A simple way to accomplish that is by adding a third stripe of a material with *positive* ζ potential. The electric field generated by the ion-exchange in the Nafion pad acting on the region of positive zeta potential would drive an electroosmotic flow now pointing outwards from the Nafion patch, redirecting the fluid flow to the following pump unit of the array as illustrated in Fig. 2b. Therefore, by repeating periodically a basic structure formed by alternating strips of deactivated Nafion (negative ζ) / Nafion / surface with positive ζ , the convective rolls could be suppressed, achieving the desired unidirectional pumping.

Accordingly, we have fabricated micropump units consisting of three adjacent strips made of deactivated Nafion, Nafion, and Al_2O_3 with 25, 25 and 30 μm width, respectively, and 500 μm long (see Fig. 3a). These elements constitute the repetitive unit in a patterned array extended in space. The self-pumping system was patterned using standard electron beam lithography, electron beam evaporation, and spin coating as detailed in Methods and Experimental Section. The process is also compatible with photolithography or the use of stencil lithography. The zeta potential of alumina was also measured at 1.10^{-4} M LiCl and pH of 5.7, verifying that it has a positive value of 17 ± 2 mV. As before, the fluid motion is followed by tracking the motion of polystyrene particle tracers in 1.10^{-4} M LiCl.

Figure 3b shows a bunch of trajectories of the polystyrene tracers when interacting with the patterned pump, proving their unidirectional motion. The average velocity of tracers along the patterned surface during the first ten minutes of actuation is depicted in Fig. 3c. In general, the tracers move with average velocities above 3 $\mu\text{m/s}$, which can be speed up at the boundaries of the different materials. The motion of particle tracers can be observed in Movie 3 of the Supplementary Information.

We have also designed another pump array by replacing the deactivated Nafion with SiO_2 structures. Silicon oxide exhibits a more negative zeta potential than the deactivated Nafion structure with a value of -66 ± 3 mV. The repetitive pumping unit consists in this case of alternating strips of SiO_2 /Nafion/ Al_2O_3 with dimensions of 25, 25 and 30 μm width, respectively, and 500 μm long (see Fig. 4a). Unidirectional fluid flow has been accomplished as can be proved from the tracer trajectories collected in Fig. 4b and

Movie 4 of the supplementary information. We have extracted the average velocity along the patterned array by evaluating the motion of the tracers during the first ten minutes of the pump actuation as depicted in Fig. 4c. Similar pump performance has been achieved as compared to the deactivated Nafion/Nafion/ Al_2O_3 with average velocities above $2\text{ }\mu\text{m/s}$ together with velocity peaks mainly at the SiO_2 /Nafion boundaries.

We have also contrasted these experimental data with finite element simulations which provides valuable information about the ion-exchange pumping mechanism. The simulations were performed using the software COMSOL Multiphysics v4.3 and the implementation details are discussed in the Supplementary Information. A micropump array of 5 repeating units, each of them composed of alternating strips of SiO_2 /Nafion / Al_2O_3 with the same stripe dimensions and zeta potentials than in the experiment, was simulated. The rest of parameters are listed in table S1 of the Supplementary Information.

Figure 5a shows the value of the horizontal component of the velocity of a polystyrene tracer particle obtained from the simulations at $3\text{ }\mu\text{m}$ above the surface. The simulations reveal the net motion of the tracer along the micropump array with average velocities above $2\text{ }\mu\text{m/s}$ and support the generation of a directional fluid flow. The tangential velocity exhibits periodic variations with large peaks at the SiO_2 /Nafion boundaries and small peaks at the Nafion/ Al_2O_3 interface. This simulation results agree qualitatively with the experimental data shown in Fig. 4c. A direct, quantitative comparison is hard to perform since the tracer particles do not follow a trajectory of constant height due to the influence of gravity, Brownian motion, and the vertical component of the velocity. The velocity peaks coincide with the regions of higher chemical gradients, as can be observed in the pH mapping of Fig. 5b. The pH map depicts an increase of proton concentration just above Nafion due to the ion-exchange building up a strong chemical gradient at the neighboring strips. This gradient generates an electric field (see Fig. S4) with a tangential component which is positive (i.e. pointing to the right) at the SiO_2 /Nafion boundary and negative (i.e. pointing to the left) at the Nafion/ Al_2O_3 border. This positive tangential electric field acting above the negatively-charged SiO_2 and negative electric field acting above the positive Al_2O_3 surface, both drive a fluid flow in the same direction (towards the right).

The streamlines of the resulting fluid velocity field are also depicted in Fig. 5b, colored by the modulus of the velocity. The fluid velocity is large and shows strong intensity variations near the surface as can be observed from the changes in color along the streamlines. The flow becomes slower and more uniform along the array at higher z distances, with average velocities still exceeding $1\text{ }\mu\text{m/s}$ at $50\text{ }\mu\text{m}$ above the surface.

Conclusions

We have introduced a new chemically powered micropump based on Nafion which is self-activated by its ion-exchange capabilities using innocuous salts as fuel. We have demonstrated high speed fluid pumping forming convection rolls but also unidirectional pumping upon adequate micro/nanostructuring of Nafion by modulating the zeta potential of the adjacent strips. Unidirectional flow is achieved with a

micropump array patterned with repetitive units consisting of alternating strips of materials with negative zeta potential (such as deactivated Nafion or SiO_2), Nafion, and materials with positive zeta potential (e.g. Al_2O_3). The interplay of the tangential component of the electric field, generated by the ion-exchange and pointing always towards Nafion, with the fine tuning of the zeta potential of the surrounding stripes redirects the fluid flow to the next micropump unit of the array, achieving the desired unidirectional flow. Numerical simulations of these pumps also support the experimental findings.

With this study we have shown the possibility of driving and guiding self-sustained fluid flows at the microscale by combining ion-exchange with a proper micropatterning of surfaces with adequate zeta potentials. This can be very important for optimizing many applications such as mass transport and material patterning at precise locations or in sensing applications. Moreover, these Nafion micropumps can be operative in a wide range of salt concentrations covering more than four orders of magnitude and can be regenerated for reusability.

This proof of concept study holds promise to expand the versatility of Nafion material from well-known application areas (e.g. fuel cells, biosensors, filtration/separation/purification technologies, novel antifouling coatings, etc.) to the appealing field of wireless micro/nanofluidic networks or self-propelled micro/nanomotors. In addition, the new strategies achieved in Nafion nanopatterning open the possibility to integrate Nafion with metals, insulators, and semiconductors in nanofabricated devices. This can pave the way to exploit the remarkable properties of this ion-exchange polymer in myriads of novel applications.

Methods

Micro-pump fabrication

1) Nafion micropump for triggering radial flows

The fabrication of Nafion micropumps started by spinning a diluted Nafion dispersion (5%) in isopropanol from a commercial Nafion dispersion in the protonated form (Aldrich, 10% in water, Eq. weight 1,100) on Si wafers modified with a 50 nm Au layer and followed by a heating step at 100 °C for 5 minutes. The spinning process was repeated to achieve typical thicknesses of about 600 nm as measured with an Atomic Force Microscope and a profilometer. After that, the Nafion film was subjected to electron-beam lithography to define a Nafion disc of 100 μm of diameter. The e-beam lithography modifies Nafion composition by the scission of $-\text{SO}_3^-$ moieties which yield to a large loss of its ion-exchange capabilities⁴⁴.

2) Nafion micropump for triggering unidirectional flows

The fabrication process starts by patterning a gold strip array on a SiO_2 wafer with strip dimensions of 50 nm thick, 50 μm wide and 500 μm long and a pitch of 80 μm . The patterning is made by standard electron beam lithography plus gold evaporation. Then the surface was subjected to an oxygen plasma

process (400 W, 2 minutes) followed by the spin coating of a 600 nm thick Nafion layer on the whole surface as described above. Taking advantage of the good adhesion of Nafion on Au, the sample was then immersed in water which removes the Nafion from the silicon parts remaining the Nafion layer only on the gold strips. A second lithographic step was performed to define an array of adjacent Al_2O_3 strips. The alumina strip was evaporated with an electron beam source and had dimensions of 30 μm wide, 500 μm long and 50 nm thick with a pitch of 80 μm . When doing this second lithographic step with the sample already containing Nafion, the development was done in methylisobutyl ketone without being diluted in isopropanol and for the lift-off dichloromethane was used instead of acetone to avoid Nafion degradation. After that an area of 25 μm wide x 500 μm long of the gold/Nafion strip was subjected to an electron beam lithography to deactivate Nafion and thus obtain the pump unit consisting of alternating strips of deactivated Nafion/Nafion/ Al_2O_3 .

In the case of the SiO_2 /Nafion/ Al_2O_3 micropump array, the fabrication process consisted of two lithographic steps. The first one was to define the Au strip patterns but in this case with a width of 25 μm and keeping the rest of the dimensions the same. The same procedure as mentioned above was followed for defining the Nafion regions on the Au strips and the alumina strips.

Zeta potential measurements of large surfaces

The zeta potential of Nafion, Deactivated Nafion, Al_2O_3 , and SiO_2 surfaces was obtained from streaming current measurement using and Electrokinetic Analyzer (EKA, Anton Paar KG, Graz, Austria). The samples were prepared on 4 x 5 cm and 0.2 cm thick polycarbonate plates. In all cases, a commercial clamping cell (Anton Paar) has been used with a PMMA sample (given by the manufacturer) facing the sample to be measured. The system was operated in an alternating pressure ramp from 0 to 300 mbar. Each measurement was the average of 8 cycles using a 10^{-4} M LiCl electrolyte solution in Millipore water.

The zeta potential has been calculated using the Helmholtz-Smoluchowski equation:

$$\zeta_{cell} = \frac{\eta}{\epsilon} \frac{L}{S} \frac{dI_{str}}{dp} \text{ eq. 1}$$

where ϵ and η are the permittivity and the viscosity of the electrolyte, respectively; L and S are the length and the cross-section of the electrokinetic channel and p and I_{str} are the pressure and the streaming current difference between both ends of the channel, respectively. The value of L/S is the same for all measurements made and has been calculated in a previous work⁵⁴: $L/S = 24.5 \pm 0.5 \text{ mm}^{-1}$.

Due to the asymmetry of the cell used, the following equation has been applied to obtain the zeta potential of each sample:

$$\zeta_{cell} = \frac{1}{2} \zeta_{PMMA} + \frac{1}{2} \zeta_{sample} \rightarrow \zeta_{sample} = 2\zeta_{cell} - \zeta_{PMMA} \text{ eq. 2}$$

where ζ_{PMMA} has been calculated with Eq. 1 using the reference PMMA sample, and its value is: -54 ± 3 mV.

Fluid Flow tracking

The fluid flow was followed by tracking the motion of 2 μm diameter polystyrene tracer particles ($\zeta = -12$ mV from Kisker Biotech GmbH & Co). Amidine modified polystyrene particles ($\zeta = 46$ mV, Invitrogen) were also used to obtain Fig. 1. The particle ζ values were obtained with a Malvern ZetaSizer. The colloidal particles were dispersed in different concentrations of LiCl salts ranging from $1.2 \cdot 10^{-6}\text{M}$ to 0.001 M . LiCl salts were chosen since previous work demonstrated that a higher electric field was generated at the Nafion interface when protons are exchanged by Li^+ ions, due to the higher difference of diffusion coefficient values between protons and Li^+ . Before the evaluation of the fluid pumping with colloidal tracers dispersed in LiCl salts, the pump devices were pre-moistened in Milli-Q water for 30 minutes. Nafion pre-wetting helps to protonate the sulfonate moieties and to minimize the fluid motion due to water uptake when inspecting the fluid pumping. The liquid cell was defined using a silicon spacer (Secure-Seal™, Invitrogen) of 9 mm diameter and capped with a cover glass. The motion of particles was optically recorded and analyzed with Diatrack software to determine their trajectory and velocity.

Declarations

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Author Contributions

M.J.E., D.R. and J.F. conceived the work. M.J.E. and D.R. designed the experiments. M.J.E. performed the experiments and analyzed the data. D.R. performed numerical simulations. A.G.R. and D.R.G. performed the zeta potential measurements of planar surfaces. All the authors discussed the results and wrote the manuscript.

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Figures

Figure 1

Radial Nafion micropumps. (a) (top) Schematic picture of the cross section of the Nafion micropumps, illustrating the pumping mechanism. The ion-exchange generates an ion concentration gradient (in green) and an electric field schematized by the red lines, mimicking those obtained from the simulations described in the Supplementary Information (Fig, S2). The charges in the deactivated Nafion illustrate the negative zeta potential of this surface (negative charges at the active Nafion interface are not shown for simplicity). The positive charges in the liquid interface denote the counterions that will move by the tangential component of the ion-exchange self-generated electric field, dragging a fluid flow towards the active Nafion disc. Near the disc edge the flow goes up by fluid continuity and finally bends outwards due to the presence of the top wall. (bottom) Top view snapshots of the actual Nafion pump taken at different heights above the surface. The polystyrene tracers dragged by the fluid approach the Nafion structure as shown in the image captured at a plane near the surface (bottom left image) and then they are lifted by the fluid and move away from the Nafion patch, as shown by the image taken at a z-plane located at 100 μm from the surface (bottom right image). (b) Average radial velocity of tracers near the surface as a function of time. Data of the different curves have been obtained by evaluating and averaging the trajectory of more than 50 polystyrene particles. The gray shaded area represents the presence of the Nafion disc from the center of the disc (0 μm) to the edge (50 μm).

Figure 2

From convective rolls to unidirectional pumping. a) Scheme of a pump made of alternating strips of deactivated and active Nafion, leading to the formation of multiple convection rolls along the patterned array. b) Scheme of the design of a pump based on the periodic repetition of a basic unit made of alternating strips of deactivated Nafion (negative ζ)/Nafion/ Al_2O_3 (positive ζ) which would lead to unidirectional fluid flow along the patterned surface. The charged interface in the Nafion has been omitted to lighten the content of the figure. The Al_2O_3 patches with positive ζ accumulate negative counterions that in the presence of the tangential component of the electric field generated by the ion-exchange will move also to the right, dragging the fluid along to the next repeating unit, achieving unidirectional flow.

Figure 3

Unidirectional pumping with deactivated Nafion/Nafion/ Al_2O_3 nanostructures. a) Patterned array of strips made from the repetitive unit composed of deactivated Nafion ($25 \mu\text{m}$, $\zeta = -37 \pm 3 \text{ mV}$) /Nafion ($25 \mu\text{m}$, $\zeta = -72 \pm 3 \text{ mV}$) / Al_2O_3 ($30 \mu\text{m}$, $\zeta = 17 \pm 2 \text{ mV}$). b) Tracer trajectories along the patterned surface proving directional motion (DN and N refer to deactivated Nafion and Nafion, respectively). c) Average tangential velocity of polystyrene tracers along the patterned structure.

Figure 4

Unidirectional pumping with SiO₂/Nafion/Al₂O₃ nanostructures a) Patterned array of strips made from the repetitive unit composed of SiO₂ (25 μm , $\zeta = -66 \pm 3$ mV) /Nafion (25 μm , $\zeta = -73 \pm 3$ mV) /Al₂O₃ (30 μm , $\zeta = 17 \pm 2$ mV). b) Tracer trajectories along the patterned surface proving directional motion (N refers to Nafion). c) Average tangential velocity of tracers along the patterned structures. Polystyrene tracers in 1.10⁻⁴ M LiCl have been used to track the fluid flow.

Figure 5

Simulations of unidirectional micropumps. a) Horizontal component of the expected velocity of a polystyrene tracer particle along the strip array composed by repetitive micropumps of SiO₂/Nafion/Al₂O₃. The tracer velocity was obtained from the simulations at 3 μm above the surface and was smoothed using a 5 μm moving average. b) pH mapping (color scale) and streamlines of the fluid flow over the first 3 repetitions of the periodic structure. The streamlines are colored by the local value of the fluid velocity, and illustrate the variations in speed caused by the local pumping triggered by the Nafion patches.

Supplementary Files

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