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ARTICLE

Asymmetric water diffusion driven nanotube actuator

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Here we report, water vapor driven actuation of polymer nanotubes, embedded in nanoporous membrane and one end attached to a surface deposited thin polymer layer. The nanotube composite shows oscillatory motion when placed near water. Permeation of water vapor through these nanotube embedded membrane is found to be direction dependent. With the water vapor as the driving force, the actuator can lift a mass 1000 times heavier than itself with a change in relative humidity of less than 40%. The actuation mechanism arises due to efficient absorption of water molecule by polymer nanotubes and its rapid evaporation through surface deposited polymer layer. This actuator can be used as artificial muscle and the direction dependent water transport may help to understand the activities of transmembrane channels and pumps of biological cells. With the aid of a nanowire generator, the oscillatory motion can be used to generate electricity too.

Introduction

Actuator materials show reversible shape and size change upon application of external stimuli, like electric voltage, light, heat or pH [1–23]. Nanoactuators are necessary for making futuristic device, like nanorobots and nanoelectromechanical systems (NEMS). Among various actuators, conducting polymeric actuators are potentially useful for making low cost, easy processing, lightweight, flexible micro electromechanical systems (MEMS), NEMS and lab-on-a-chip systems. The actuation mechanism of most of the conducting polymer actuators is a bulk phenomenon and based on electrochemical dopant intercalation. Water driven actuation has also been observed in several systems [14–18], where water causes swelling of the systems. The actuator reported here, rely on the asymmetric absorption and desorption of water by nanotube and thin film of polymer. The actuator is made of Polyaniline (PANi) nanotubes embedded in nanoporous (polycarbonate) membrane, and one end of the nanotubes is attached to a surface deposited thin PANi layer. The nanotubes embedded membrane (NEM) shows oscillatory motion when placed near water in open environment. In closed environment, the composite membrane remains rolled up in dry condition and gradually unfolds with increasing humidity. In presence of humidity gradient, water moves faster through the NEM if the

open nanotube side faces the high humidity region. This direction dependent flow of water is reminiscent of water activity of transmembrane channels and pumps of biological cells [24]. The oscillatory motion arises due to efficient absorption of water by the nanotubes and rapid evaporation through the surface deposited PANi layer. In a controlled environment, the actuator can lift objects 1000 times heavier than itself with a relative change of humidity as small as 40%.

Sample fabrication

NEMs were made by synthesizing PANi nanotubes inside nanoporous polycarbonate membrane through chemical route. Freshly distilled aniline was used as monomer and FeCl₃ as oxidizing agent. Polycarbonate membranes (Wattman Company) of various pore diameters ranging from 15 nm to 200 nm were used as templates (a representative SEM image of bare polycarbonate membrane having 50 nm pore diameter has been shown in Fig. 1(a)). The membrane is placed with a rubber O-ring and clip between a two-compartment glass cell and monomer was added in one compartment and oxidizing agent in other compartment. Inside the pores, monomer reacts with the oxidizing agent and form polymer chains, which then deposited to the negatively charged pore wall to make the

nanotubes. With increasing deposition time the inner diameter of the nanotubes decreases. However, for long deposition time

Care has been taken not to remove the surface deposited layer. The samples are then vacuum dried for 2 days and ready for further study. To determine the nanotube quality and yield we have done scanning electron microscopy (SEM). The nanotube embedded polycarbonate membrane first attached to the SEM sample holder, then part of it is mechanically polished to remove the surface deposited layer from that portion, and finally Chloroform is added with a cotton swab to remove the polycarbonate membrane.

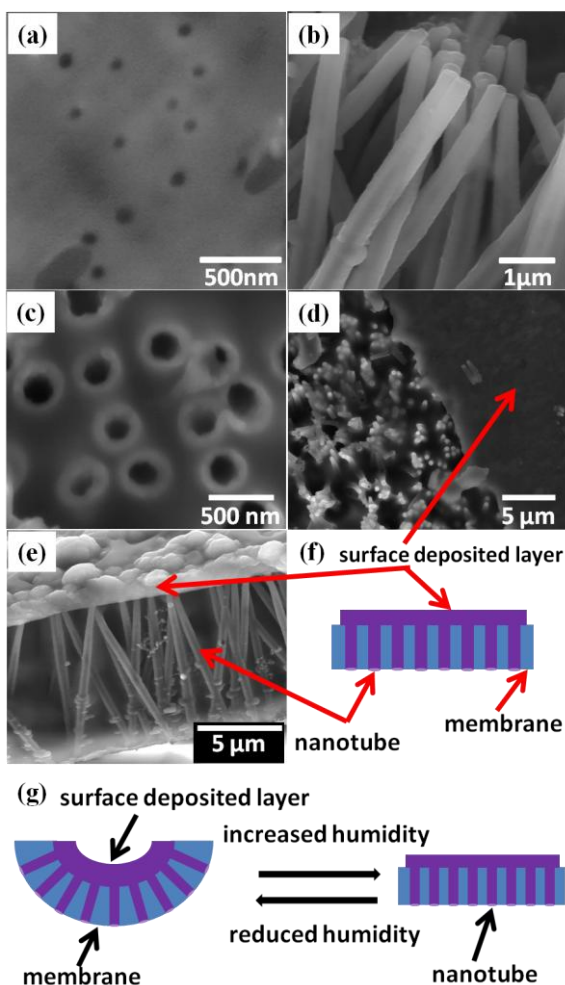


Fig. 1 (a) SEM image of a typical polycarbonate membrane having 50 nm pore diameter. (b) PANi nanotube synthesized using 200 nm pore diameter membrane. Image taken after removing the polycarbonate membrane. (c) Higher magnification image showing open end of the nanotubes. (d) Low magnification image from top, showing nanotubes and part of the surface deposited layer. (e) Cross-sectional view clearly shows that nanotubes are attached to the surface deposited layer. (f) Schematic of the NEM indicating nanotubes and surface deposited layer. (g) Schematic of the actuation motion of NEM with changing humidity. NEM gets unrolled with increasing humidity and rolls up with decreasing humidity. In the rolled condition, the surface deposited layer remains inside.

(several hours) we found that the pore does not completely filled up and remains hollow. The reason is that, a thin polymer layer deposited on the surface of the membrane in the monomer side, and as time goes its thickness increases and blocks the pore, thus prevents further reaction. This thin surface deposited layer plays an important role in the observed actuation. After the deposition is completed, the membrane containing nanotubes were washed several times with deionized water.

Results and discussion

In Fig. 1(b) we showed representative SEM image of the PANi nanotubes synthesized using 200 nm pore diameter membrane. Image was taken after completely removing the polycarbonate membrane. In Fig. 1(c), a higher magnification image of the other side of the NEM shows that, the pores of the nanotubes are not completely filled. Image was taken after partially removing the membrane from top. Fig. 1(d) shows low magnification image of nanotubes and part of the surface deposited layer. A cross-sectional view of the NEM, after dissolving the membrane has been shown in Fig. 1(e). In Fig. 1(d) and (e), the nanotubes and the surface deposited PANi layer are clearly visible. Schematic of the NEM composed of nanotube, surface deposited layer and membrane is shown in Fig. 1(f). The bottom side of the NEM schematic looks similar to Fig. 1(c). If the surface deposited PANi layer is not removed, then the membrane containing nanotubes remains rolled up in dry condition (in reduced humidity environment) and the surface deposited PANi layer resides inside. In presence of water vapor, the NEM starts to unfold and at relatively high humidity it becomes flat (see Fig. 1(g) for a schematic).

In Fig. 2(a), we showed gradual shape changes of NEM (synthesized using 200 nm pore diameter polycarbonate membrane) as a function of humidity. In a controlled environment, the NEM shows very reproducible movement and it can bend more than 360° (see Fig. 2(b)) depending on the relative humidity (in Fig. 2(a) the NEM is completely rolled up below $\sim 25\%$ humidity). To show this, we cut a NEM in the shape of flower and captured its shape change, in a video, with changing humidity (see supplementary Video-1). At $\sim 60\%$ humidity the “flower” remains open and as the humidity decrease, it closes and the process is reproducible over years. In another video (see supplementary Video-2), we have shown that the response time is less than 1sec. The actual determination of response time is difficult, as it requires very fast (faster than the relaxation time) change of environment humidity. The same video also shows that the response is reversible. Fig. 2(b) shows bending angle as a function of relative humidity for 200 nm pore diameter NEM. We found that for a particular humidity, larger pore diameter NEM bends slightly more (see Fig. 2(c)). For a typical NEM the bending direction is determined by the inhomogeneity in the thickness of the surface deposited layer and asymmetry in the shape of the NEM. If the thin PANi layer from the surface of the NEM is removed by mechanical polishing, then the NEM does not rolled up on drying and no actuation is observed. The actuation stops after applying a thin layer of grease either on the surface deposited layer or on the other side (open nanotube side). In addition, a bare polycarbonate membrane does not show any actuation in presence of water. To determine the necessity of the nanotubes in the observed actuation mechanism, we deposited PANi thin film of various thicknesses (starting from

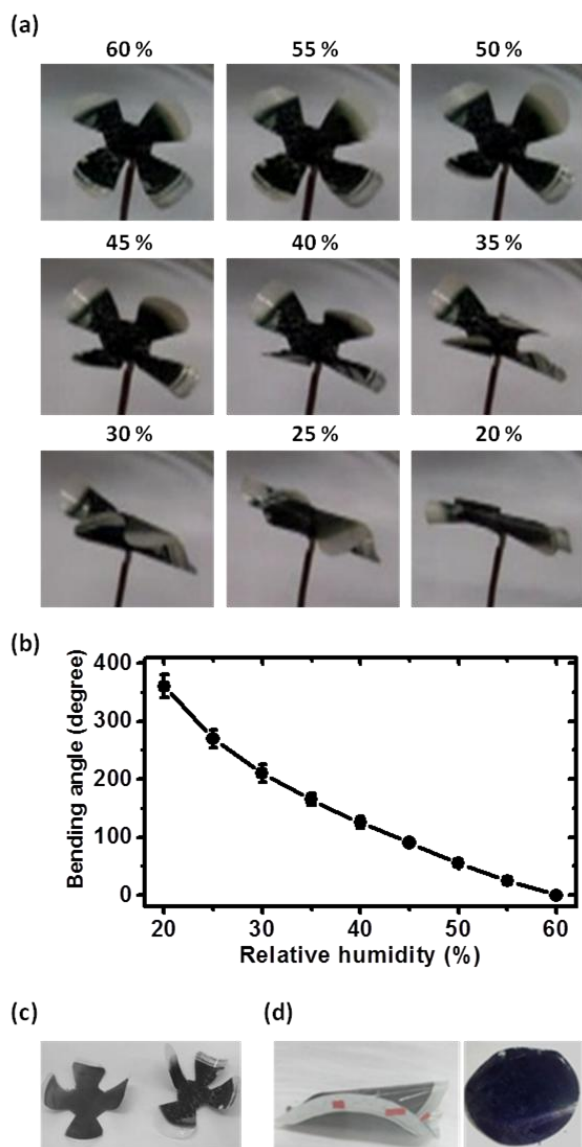


Fig. 2 (a) Gradual shape change of NEM (made from 200 nm pore diameter membrane and cut into a shape of flower) with reducing humidity. At $\sim 60\%$ humidity, it remains flat, with decreasing humidity it rolled up. (b) Bending angle as a function of relative humidity is shown for 200 nm pore diameter NEM. (c) Bending of 200 nm (right) and 15 nm (left) pore diameter NEMs are shown for 50% relative humidity. (d) NEM made of 200 nm pore diameter (left) and PANi film deposited on same thickness polycarbonate membrane (right). The second one does not show any actuation.

100 nm to few microns) on a polycarbonate membrane of same thickness and exposed it to water. However, we do not find any actuation in this case. In Fig. 2(d) we have shown a rolled up NEM (right panel) in the reduced humidity condition (the red markers indicate the open nanotube side, surface deposited layer remains inside) and the right panel shows a $\sim 1\ \mu\text{m}$ thick PANi film deposited on the 15 nm pore diameter polycarbonate membrane. In the second case, the deposition of PANi film is done in such a way (monomer and oxidizing agent added on the same cell and polymerization takes place outside the pores) that

nanotubes do not form (polymer does not go inside the pores) and this membrane does not show any actuation with changing humidity.

It is clear from the above discussion that, water absorption is responsible for the observed actuation of NEM. The PANi nanotubes and the surface deposited layer absorb water, which increases the volume of PANi as a result, the rolled NEM stretched. We have measured the water intake of the NEM as a function of humidity for various diameter polymer nanotubes. Fig. 3 shows that water intake increases linearly with increasing relative humidity for all the NEMs. To determine the amount of PANi in completely dry NEM for a particular nanotube diameter, we fit the data (shown in Fig. 3) to a straight line, thus calculated the weight of the NEM without any absorbed water and the weight of the corresponding bare membrane is subtracted from it.

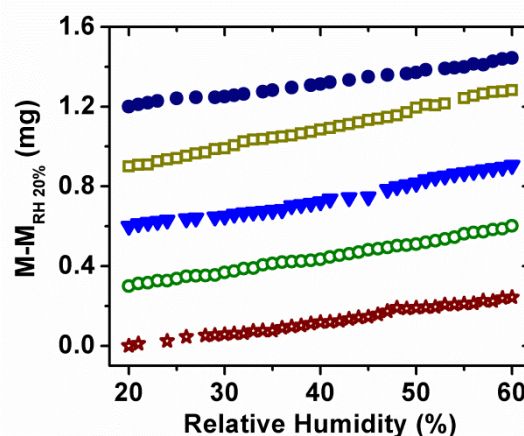


Fig. 3 Water intake of NEM as a function of humidity for various diameter nanotubes (15, 30, 50, 100 and 200 nm from bottom to top, other than 15 nm all data were shifted vertically for clarity). Weight of the NEM at 20% humidity is taken as reference for a particular diameter nanotube.

Fig. 4(a) shows the experimental schematic used to measure the force exerted by a NEM actuator as a function of humidity. The NEM was cut in to a rectangular strip (4 mm wide and 15 mm long) and a force sensor was attached to it and placed inside a glass enclosure, equipped with a humidity and temperature sensors. The humidity was controlled by introducing either dry nitrogen gas or water vapor. The force measurement was done by reducing the humidity from 60% (freestanding NEM remains stretched) to 20% (freestanding NEM becomes rolled up). With decreasing humidity, as the water expelled from the NEM it tries to roll up and exerts a tensile force. From a stretched condition (at 60% relative humidity), it can lift up to 160 mg mass if we reduce the humidity to 20%. In Fig. 4(b) we showed mass lifted by a typical NEM, having 200 nm pores, as a function of mass of the expelled water. As we have already mentioned, polycarbonate membrane alone does not show any actuation, so the water absorption and desorption by PANi nanotubes and the surface deposited film present in NEM are responsible for the observed actuation. We found that, the ratio of the mass lifted to the mass of water expelled could be as high as 1000 times. Compared to the mass of the polymer (PANi) material present in NEM, it can

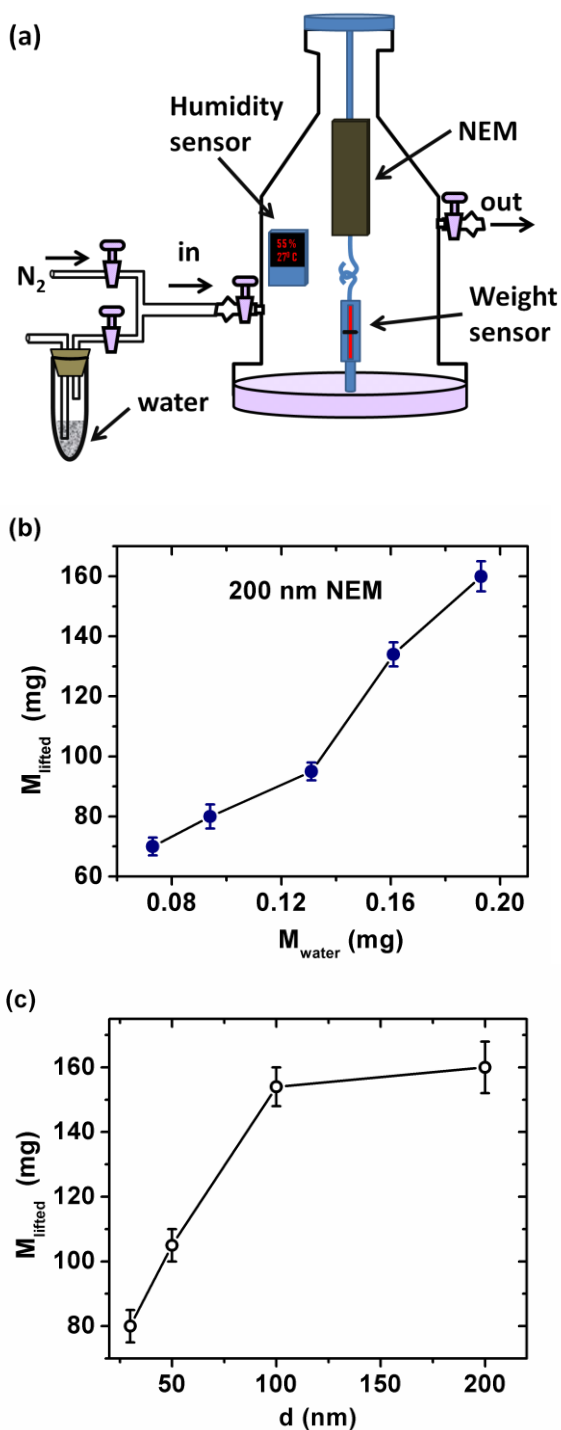


Fig. 4 (a) Schematic of the set up used for measuring the force exerted by NEM actuators as a function of humidity. The humidity is controlled by sending dry nitrogen gas or water vapor. (b) Mass lifted by a rectangular piece (15 mm by 4 mm) of NEM, made of 200 nm diameter nanotubes, as a function of amount of water expelled. (c) Maximum mass lifted by the same size (15 mm by 4 mm) NEM having different pore diameters (humidity reduced from 60% to 20%).

lift ~1000 times heavier mass than its own. Fig. 4(c) shows maximum mass lifted by NEM made of various pore diameter

membranes. It is evident that below 100 nm, the maximum mass lifted, decreases significantly with decreasing pore size. This is probably, narrow pore gets quickly filled on the surface deposited layer side and PANi film remains thin (we found that for 15 nm and 200 nm pore the thicknesses of PANi films are ~100 nm and ~1 μm respectively).

Interestingly, it has been observed that in open environment, if the NEM is placed near a water container, then it repeatedly become unrolled and rolled causing an oscillatory motion, we call it "breathing" of NEM (see supplementary information: Video-3). Breathing is not observed in the closed environment or if the water container is placed far away. This indicates fluctuation of humidity in the local environment is needed to observe breathing.

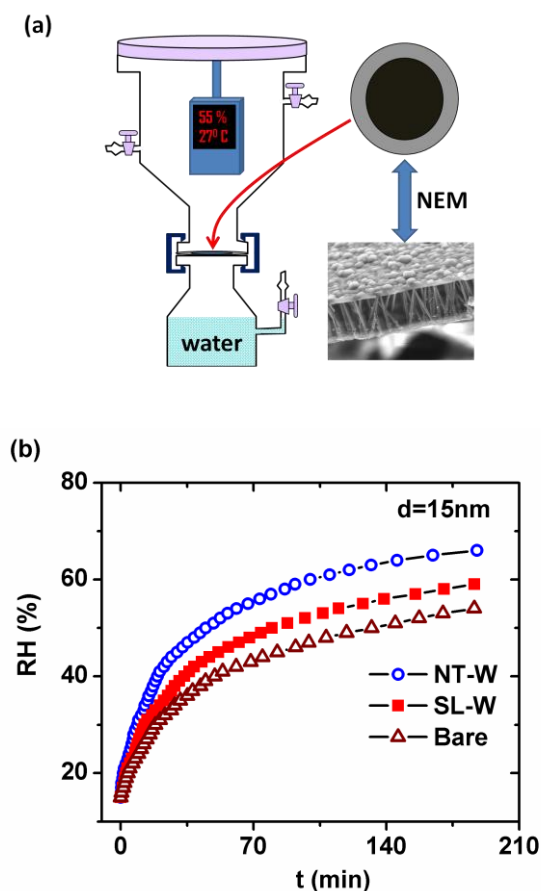


Fig. 5 (a) Schematic of the setup used to study the water vapor permeation through the NEM. Water molecule permeates through the NEM and increases the humidity in the upper container, which is then monitored as a function of time. (b) Change of humidity in the upper container has been shown as a function of time for 15 nm bare membrane (open triangle), NEM with surface deposited layer side facing the water (SL-W) in the bottom container (solid square) and NEM with open nanotube side facing the water (NT-W) shown by symbol open circle

In the open environment, humidity near the water container fluctuates with time, so the breathing may be due to the absorption and desorption of water molecule by the surface

deposited layer of the NEM. If this is the reason, then the PANi nanotubes should not have any effect on the breathing. However, we noticed that breathing stops after applying a thin layer of grease to block the pores of the nanotubes on the other side (opposite to the surface deposited layer side). We also do not see any breathing in thin film of PANi deposited on flexible substrate. If we apply grease on the surface deposited layer side, then also we do not see any breathing. This clearly shows that, nanotubes and the surface deposited layer both play role in the breathing and they probably have different water absorption-desorption characteristics.

If we consider that, the nanotubes absorb water efficiently than the surface deposited layer, and as the absorbed water gradually reaches the surface deposited layer, it expands and NEM starts to unroll with increasing amount of water. Due to fluctuation of humidity (a slight decrease in humidity) in the local environment, if water desorbs quickly from the surface deposited layer then NEM will roll up. However, it could be the other way too, that is, the surface deposited layer absorbs water-vapor efficiently with increasing humidity and water desorbs quickly through the nanotubes with decreasing humidity. Both the mechanisms will give breathing of NEM.

We did the following experiment to determine the absorption and desorption efficiency of nanotube and surface deposited layer in presence of humidity gradient. We measured the water vapor permeation through the NEM. In Fig. 5(a), we have shown a schematic of the experimental set up used for the water vapor permeation measurement. The NEM is placed in between two glass container with o-ring and clips. The lower container partially filled with water. Before starting each measurement, the upper container is flushed with dry nitrogen to remove the moisture as much as possible. A humidity sensor (minimum sensitivity less than 18 %) is placed in the upper container, which measures the change of humidity, thus gives an indication of the amount of water vapor present in the upper container. After mounting a particular pore diameter NEM, we flush the upper chamber with dry nitrogen until the relative humidity goes below 18 %, then we stop introducing dry nitrogen and start measuring the increase in relative humidity as a function of time. During the experiment, care has been taken to keep the temperature of the environment constant. In Fig. 5(b), we showed one such representative data for a typical NEM measured at 27^o C. It is interesting to note that, when surface deposited side of the NEM is facing the water container, the relative change of humidity in the upper container is slow with time compared to the nanotube side facing the water. This indicates that open nanotube side absorbs the water vapor more efficiently and the water evaporates from the surface deposited layer easily compared to the open nanotube side. This explains the observed breathing of NEM. Interestingly, water permeation rate for both the cases are high compared to a bare membrane, this is probably due to the hydrophilic nature of the polymer nanotubes. It can also be due to the small pore diameter of the channels, because fluid moves faster as the pore gets narrower [25–27].

Quick and efficient absorption of water by the nanotubes is probably due to the capillary effect [25–31]. The absorbed water reaches the surface deposited layer and with increasing amount of absorbed water, the NEM gets unrolled. Any small fluctuation (decrease) of humidity cause the water to evaporate quickly from the surface layer (due to the capillary effect water

cannot evaporate quickly from the nanotubes) and the NEM gets rolled up. In closed environment, the humidity does not fluctuate and the NEM does not show the oscillatory motion. Because of the capillary effect, water cannot easily evaporate from the nanotubes hence, with decreasing humidity the surface deposited side remains inside when the NEM gets rolled (water from the surface evaporates easily and the volume reduction is large compared to nanotubes).

Conclusions

In conclusion, we have shown actuation of polymer nanotube embedded membrane. The actuation mechanism is based on the asymmetric diffusion of water through the NEM. These actuators show very long lifetime and high stability. We found that, more than 5 years old NEM shows actuation without any significant decrease of performances. These actuators may find potential application in artificial muscle, separation technology in chemical and biological field and drying technology. The asymmetric flow of water molecule through the NEM can be used as a model system to understand the ion channels and ion pumps observed in biological systems [24]. Attaching a nanowire nanogenerator [32–34] with this polymer actuator and placing it near a water bath in the open environment, the oscillatory motion can generate electricity also.

Notes and references

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Electronic Supplementary Information (ESI) available: Three videos showing humidity dependent actuation and oscillatory motion near a water container of the nanotube embedded membrane. See DOI: 10.1039/b000000x/

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TOC

Polymer nanotubes attached to a surface deposited thin polymer layer show actuation due to asymmetric water vapor diffusion.

