

Supplementary Information

Facile Fabrication of Dual-Conductivity, Humidity-Responsive Single-layer Membranes: Towards Advanced Applications in Sensing, Actuation, and Energy Generation

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1. Supplementary Figures and Tables

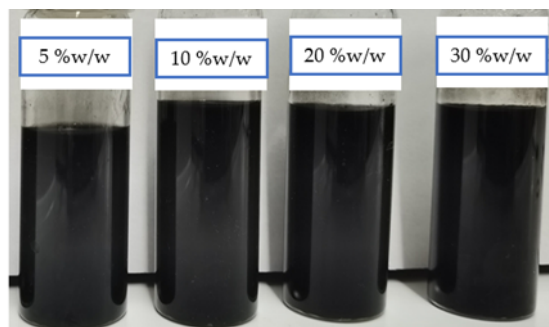


Figure S1. Images of P(SSNa-co-GMA40)/PAA 90/10 wt% aqueous composite solutions with different wt% content of CNTs.

Table S1. Blend composition of the prepared membranes.

Polymer Blend	Composition wt%	CNTs wt% of P(SSNa-co-GMA40)	Total CNTs content wt%	Film
P(SSNa-co-GMA40)/PAA	90/10	5	4,3	A5
P(SSNa-co-GMA40) /PAA	90/10	10	8,3	A10
P(SSNa-co-GMA40) /PAA	90/10	20	15,3	A20
P(SSNa-co-GMA40) /PAA	90/10	30	21,3	A30

Table S2. Swelling ratio (%) and soluble fraction (%) of the prepared membranes after treatment at RT and 120 °C.

Membrane	Swelling %		Soluble Fraction %	
	RT	120 °C	RT	120 °C
A0	2466	377	13.7	5.7
A5	1388	870	19.5	11
A10	1116	323	19.8	2
A20	714	195	19.4	0
A30	585	147	19.2	0

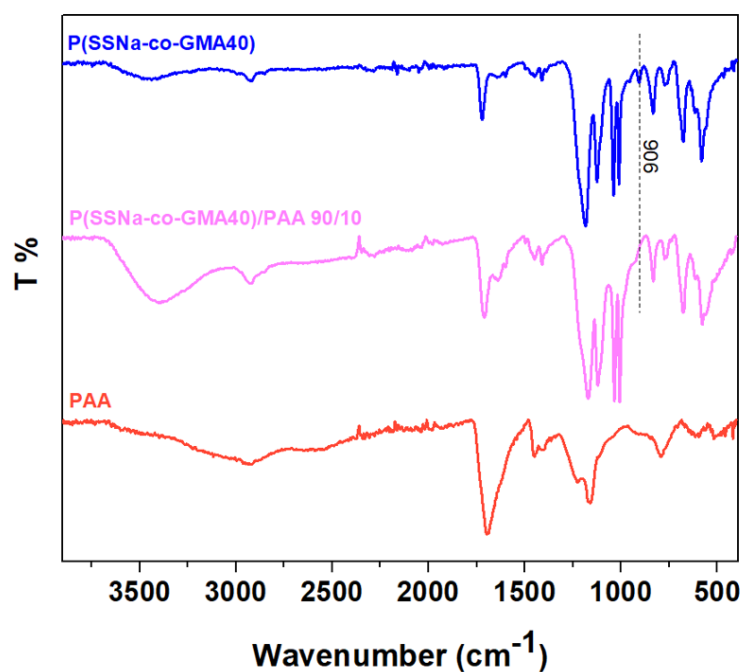


Figure S2. ATR-FTIR spectra of the cross-linked membrane P(SSNa-co-GMA40)/PAA 90/10 w/w and the P(SSNa-co-GMA40) and PAA as well, for comparison.

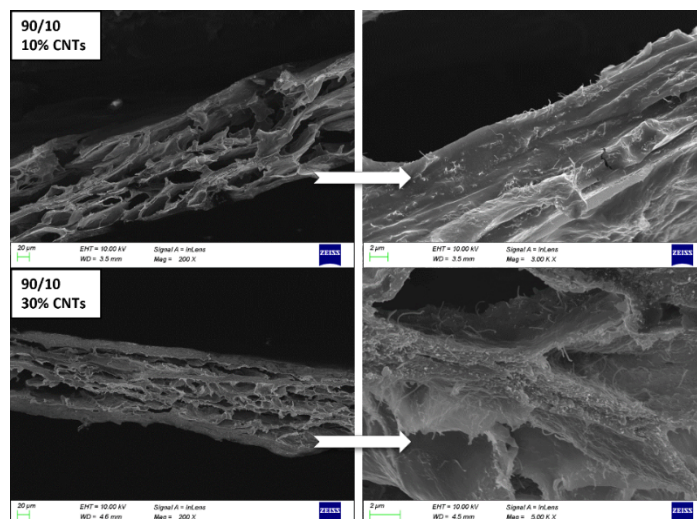


Figure S3. SEM images (cross-section) of cross-linked composite membranes with 10 and 30 % CNTs loadings.

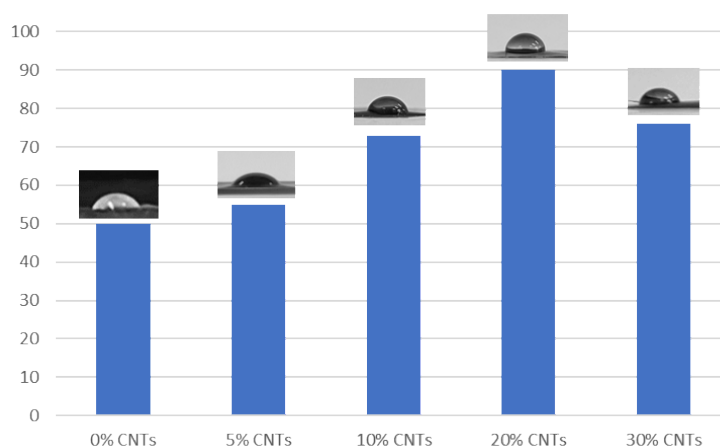


Figure S4. Contact angle measurements of the crosslinked membrane without CNTs (0%) and the respective membranes with 5, 10, 20 and 30% CNTs.

Incorporating the partially carboxylated CNTs into the polymer solution leads to alterations in surface properties, consequently impacting contact angles as shown in **Figure S4**. The introduction of carboxyl groups enhances the compatibility of CNTs with the aqueous environment, facilitating improved dispersion within the polymer matrix. This integration induces shifts in surface energy and wettability of the resulting material, influencing contact angles, a crucial parameter for comprehending interactions at interfaces. As the percentage of nanotubes increases, contact angle values rise due to the hydrophobic nature of the CNTs. However, when the nanotube percentage reaches 30%, a slight decrease in the contact angle is observed, suggesting a potential surface roughening effect that affects these values.

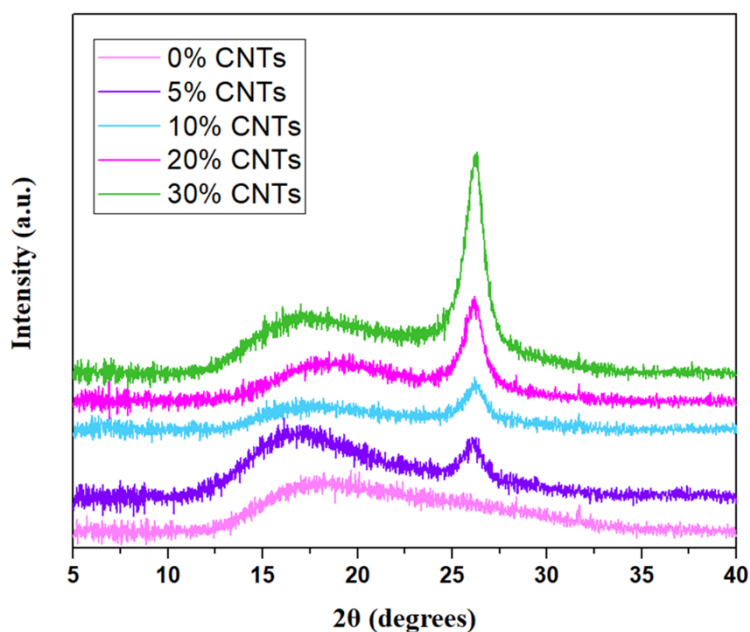
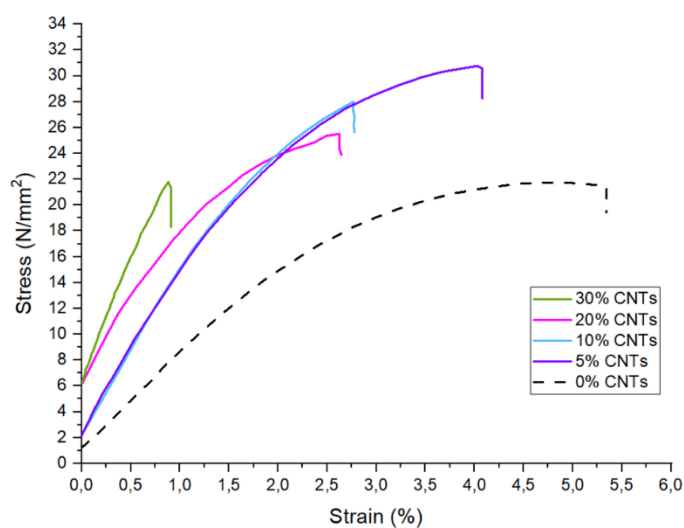


Figure S5. XRD spectra of the membranes with different loading of CNTs (0-30%).



Film (% CNTs loading)	E (MPa)	σ_b (MPa)	ϵ_b (%)
P(SSNa-co-GMA40)/PAA (0% CNTs)	782±21	21,5±1,0	5,5±1,5
P(SSNa-co-GMA40)/PAA/CNTs 5%	959±158	30,7±3,2	4,2±0,6
P(SSNa-co-GMA40)/PAA/CNTs 10%	1122±167	28,3±5,5	2,7±0,7
P(SSNa-co-GMA40)/PAA/CNTs 20%	1214±229	25,6±5,0	2,6±1,1
P(SSNa-co-GMA40)/PAA/CNTs 30%	2044±320	21,9±2,5	0,9±0,3

Figure S6. Mechanical performance of the membranes. Typical tensile stress vs. strain curve of the crosslinked composite membranes. Young's Modulus (E), tensile yield strength (σ_b) and elongation at break (ϵ_b) are displayed in the table inset.

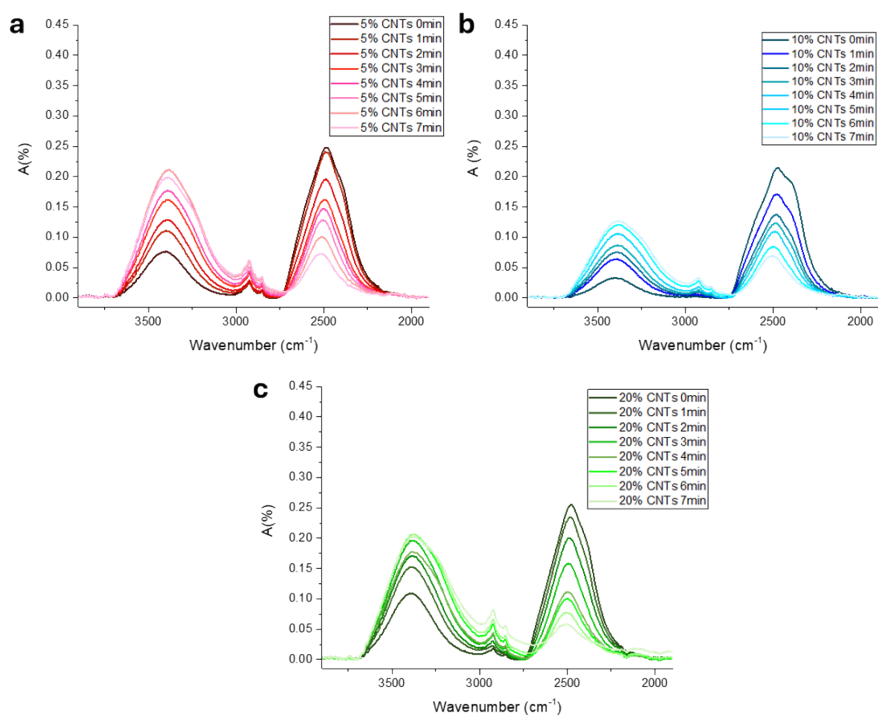


Figure S7. ATR-FTIR spectra of the membranes, showing H/D exchange. Membranes (90 μm thickness) with 5 wt% (a), 10 wt% (b) and 20 wt% (c) CNTs are depicted. Top to bottom: after 0, 1, 2, 3, 4, 5, 6, and 7 min of exposure with D_2O .

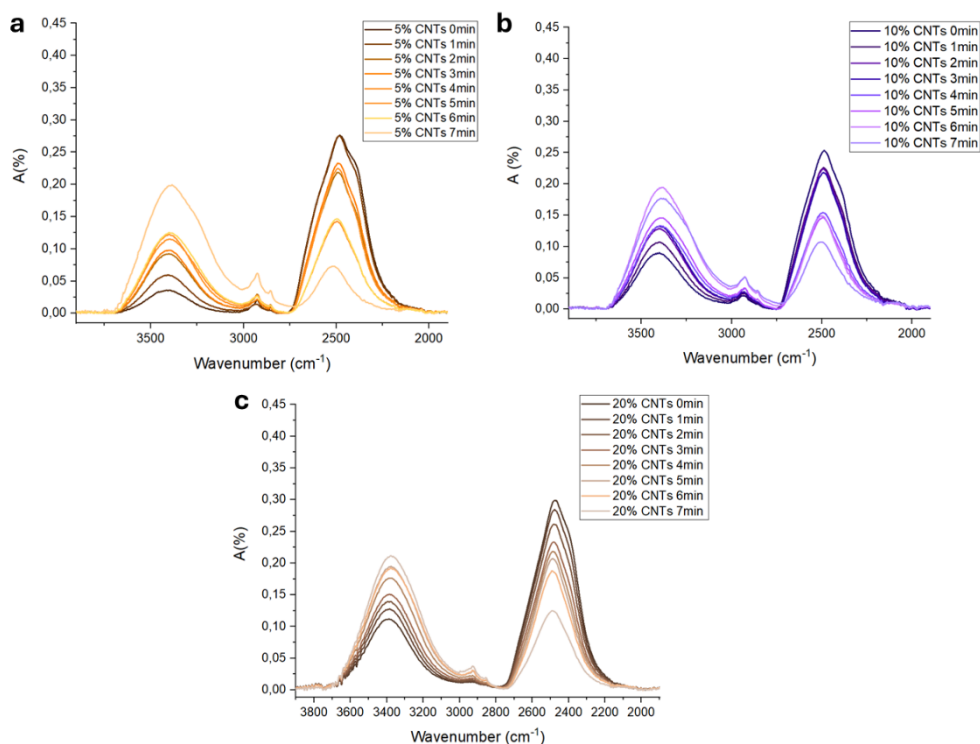


Figure S8. ATR-FTIR spectra of the membranes, showing H/D exchange. Membranes (120 μm thickness) with 5 wt% (a), 10 wt% (b) and 20 wt% (c) CNTs are depicted. Top to bottom: after 0, 1, 2, 3, 4, 5, 6, and 7 min of exposure with D_2O .

2. Experimental Section/Methods

Materials: Glycidyl methacrylate (GMA), sodium 4-styrene sulfonate (SSNa), poly(acrylic acid) (PAA), the initiator azobisisobutyronitrile (AIBN), as well as deuterium oxide (D_2O) and deuterated chloroform ($CDCl_3$) were purchased from Sigma-Aldrich and used as received. Lithium chloride (LiCl), calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$), sodium bromide dihydrate ($NaBr \cdot 2H_2O$), sodium chloride (NaCl), and potassium nitrate (KNO_3) were purchased from Aldrich. N,N-dimethylformamide (DMF), chloroform ($CHCl_3$), ethyl acetate, acetone and hexane were purchased from Fischer and used as received. Dimethyl sulfoxide (DMSO) and ethanol were purchased from Honeywell. Ultra-pure water was obtained by means of an SG apparatus water purification unit. Carboxylic multi-walled carbon nanotubes (> 95 wt % purity; carboxyl content: 0.7 wt %) were supplied by Cheap Tubes. The CNTs are 15–20 μm in length and 30–50 nm in outer diameter.

Synthesis of copolymers: The water-soluble copolymer poly (sodium 4-styrene sulfonate-co-glycidyl methacrylate) with 40 %mol GMA P(SSNa-co-GMA40) was synthesized in accordance with an earlier experimental procedure via free radical polymerization using AIBN as initiator and DMSO as solvent.^[1]

Preparation of composite membranes: Initially, MWCNTs-COOH dispersions were prepared as follows: 1% w/v polymeric solutions of P(SSNa-co-GMA40) were first prepared and then the appropriate amount of carbon nanotubes was added (5-30% wt. of the polymer composition), as shown in Table 1. The solutions were sonicated 3 times for 10 minutes each and left under mild stirring overnight. Afterwards, the polymer/CNTs dispersions were mixed with polyacrylic acid (PAA aq. solution 10% w/v) in a blend composition P(SSNa-co-GMA40)/PAA of 90/10 w/w and left in polystyrene dishes at room temperature to dry. Finally, the formed membranes were thermally treated at 120 °C for 18 hrs to allow the crosslinking reaction between the epoxy group of GMA and the carboxyl groups of both PAA and MWCNTs-COOH to proceed.

Scanning electron microscopy (SEM) examination: Scanning electron microscopy (SEM, Zeiss SUPRA 35VP and JEOL 6300, Tokyo, Japan, instruments equipped with an X-ray Energy Dispersive Spectrometer, EDS) was performed to investigate the membranes' cross-section morphologies. The samples were sputtered with gold to produce electric conductivity. Before the examination the membranes were swelled in water for several hours and then freeze-dried, to maintain their morphology.

X Ray Diffraction (XRD) analysis: The composite membranes' structure was examined using a Bruker D8 Advance X-ray powder diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm). The measurements were conducted within the 2θ angle range of 5–40 deg.

Contact-angle measurements: The contact angle measurements were carried out by the sessile drop method. Specifically, a 10 μ L droplet of ultra-pure water was pipetted onto the surfaces of the membranes and contact angles were measured using the ImageJ software.

Swelling Test: Small pieces of both crosslinked membranes, which were heated to 120 °C and non-crosslinked membranes (kept at room temperature-RT), were immersed in glass vials filled with water and left at room temperature for 24 hrs. Visual inspections were carried out to assess the appearance of the samples and the swelling ratio of the membranes was quantified through a gravimetric analysis.

Tensile measurements: Mechanical properties of cross-linked membranes were measured using a Precision Universal/Tensile Tester, Autograph AGS-X, Shimadzu (Shimadzu. Asteriadis S.A., Athens, Greece), equipped with 10KN load cell, at a cross speed of 10 mm/min, at room temperature and relative humidity \sim 45 %. The Young's Modulus E, tensile yield strength (σ_b) and elongation at break (ϵ_b) were measured according to the specifications of the American Society for Testing and Materials (ASTM) D638. The average value and s. d. were calculated from a minimum of four samples.

Examination of membrane wetting/dewetting by ATR-FTIR spectroscopy: ATR-FTIR spectra of the membranes were recorded using a Bruker Platinum ATR-FTIR spectrometer. After immersing the membrane sample in D₂O for a duration of 10 seconds, it was then removed from the D₂O solution and promptly dried with tissue paper to ensure no residual D₂O drops remained on its surface. Subsequently, the initial ATR spectrum was recorded. The sample was then held in the air using tweezers, and its ATR spectrum was recorded at one-minute intervals. Each individual ATR scanning process took approximately 10 seconds to complete.

Bending angle-Curvature measurements: The experimental setup involved the use of two vertical rectangular glass slides placed in parallel. On one of the slides, a membrane strip was affixed at the lower end. The opposite slide was covered with a damp filter paper, positioned parallel to the hanging membrane strip. The moisture content on the filter paper was determined through the oven dry method, resulting in a value of approximately 62%. This configuration allowed the membrane strip to move freely. When the wet filter paper approached the strip, it induced bending in the membrane strip. Once a stable maximum

bending state was achieved, photographs were taken to calculate the bending angle using the ImageJ software. Finally, the curvature, denoted as K , was computed using the formula: $(K = \alpha * \pi) / (180^\circ * L)$, where α ($^\circ$) represents the bending angle, and L (cm) corresponds to the length of the free section of the curved membrane.

Conductivity Measurements: The electrical properties of the as-prepared humidity sensors were characterized by a PGSTAT 302N electrochemical workstation. The electrical performance of the samples under different humidity conditions was recorded by placing them in many sealed bottles with saturated aqueous solutions of different salts at 23 °C under an applied voltage of 1 V, respectively. The relative humidity in the sealed bottles was achieved by using saturated solutions of LiCl, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NaBr} \cdot 2\text{H}_2\text{O}$, NaCl and KNO_3 to have 11%, 29%, 57%, 75% and 95% RH respectively. The dry environment (corresponding to 0% RH) was achieved by using a sealed bottle with P_2O_5 . In order to ensure proper hydration of the membranes before measurement, all samples were first dried and then left in the appropriate environment for at least 30min.

Electrochemical Impedance Spectroscopy Measurements: For the fabrication of the electrodes, gold on PET substrates were cleaned with ethanol, dried at room temperature and coated with Kapton tape. Then, gold/PET substrate was laser cut (VLS 2.30, Universal Laser Systems) to shape circular electrodes of 8 mm with a rectangular surface for the electrical connection (**Figure S9**). Finally, Kapton tape was removed from the active areas and washed with deionized water to remove residues. The film was also laser-cut before the assembly of the CNT films within the EIS cell. The bulky film was laser cut in 8 mm circular shapes, using 2% of power, 13% speed, 1000 DPI and 1.3 mm of z-height. The electrochemical impedance spectroscopy (EIS) measurement was carried out in a homemade device with a coin-like cell shape. The previously described 8 mm radio gold/PET laser cut was used as electrodes. Kapton tape was used for the passivation of non-active areas. The CNT film was placed between the two coplanar gold electrodes, ensuring the contact and the electrical flow of current throughout the CNT film. The plotted measurement, as well as standard deviation, were obtained from three different films analyses. Besides, the material's performance was compared between dry and moisturized (denoted as wet). For the experiment, EIS measurement was performed with an electrochemical workstation Autolab MSTAT204 Potentiostat/Galvanostat. The measurement was acquired in frequency range from 0.1 to 100000 Hz using an amplitude value (V_{rms}) of 0.3V. CNT films were moisturized inside of a

vapor chamber (**Figure S10**). 100ml of water was warmed at 80°C and stirred at 200 rpm with the chamber partially sealed, until 90% of relative humidity and 60°C temperature was reached. These conditions are considered as the steady state of the system, and were maintained constant for more than 30 min. Then, the CNT films were placed inside the chamber for 20 min. Afterward, the film was directly assembled between the two coplanar electrodes and the EIS measurements were performed.

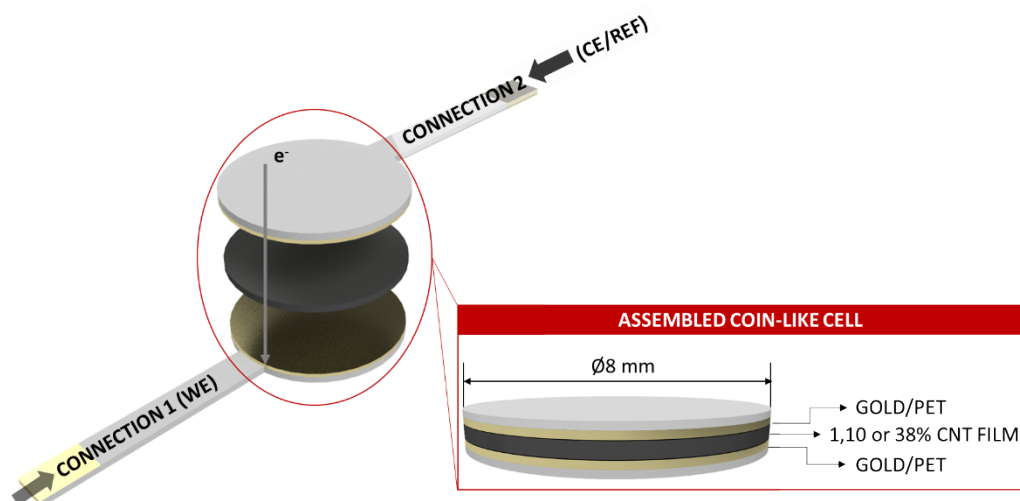


Figure S9. Cell used for the EIS measurements.

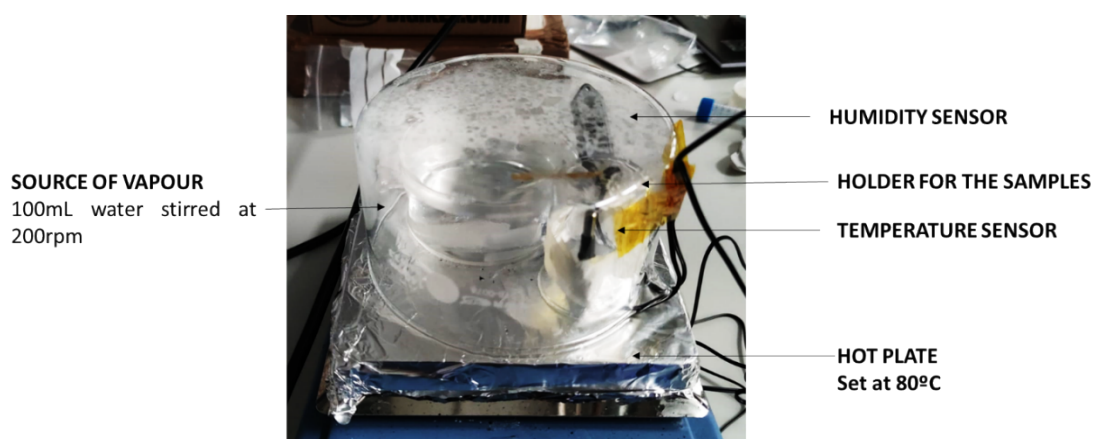


Figure S10. Full experimental setup for the EIS measurements of the wet membranes.

Humidity sensor characterization: To probe the possibility of the composite membranes to be used as humidity sensors, strips of the appropriate membrane were cut to about 2x1 cm dimensions and were subsequently tested as humidity sensors. In order to fabricate the circuits to demonstrate the strips' potential as sensors and switches, swallow tailed clamps were used, along with several LEDs, copper wires, steel alligator-type clamps, a multimeter, a

power source, and conducting tape. For the first experiment, a strip of the appropriate composite membrane (with 0%, 5%, 10%, 20% and 30% CNTs) was laid on a non-conducting surface. Next, two steel clamps were used, that were connected via copper wires to an LED and a power source. At ambient humidity, when the two steel clamps were brought to contact with the strip, the circuit was closed, and the LED connected to the other side of the circuit turned on, in the case of the membranes with 10%, 20% and 30% CNTs. For the next experiment that demonstrates their application as humidity-driven switches, a strip of 1x2 cm dimensions was affixed from one side on a swallow tail clamp, while the other end was left free. Close to the free end of the membrane, the electrode of an LED was left free, while the other side of the LED was connected to a power source via copper wires. For the last experiment, demonstrating their use as power generators, a 1x2 cm membrane was fixed on both sides by PDMS. Both sides of the membrane were wrapped in aluminum foil. On each side, steel alligator-type clamps connected to a multimeter were fixed, to measure the voltage through the membrane. Humidity was transferred on the membrane via plastic tubes from a flask of boiling water.

References

- 1 I. Tzoumani, G.C. Lainioti, A.J. Aletras, G. Zainescu, S. Stefan, A. Meghea, J.K. Kallitsis. *Materials* 2019, **12**, 4067.