Nanodancing with Moisture: Humidity-Sensitive Bilayer Actuator Derived from Cellulose Nanofibrils and Reduced Graphene Oxide

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Bilayer actuators, traditionally consisting of two laminated materials, are the most common types of soft or hybrid actuators. Herein, a nanomaterial-based organic–inorganic humidity-sensitive bilayer actuator composed of TEMPO-oxidized cellulose nanofibrils (TCNF-Na⁺) and reduced graphene oxide (rGO) sheets is presented. The hybrid actuator displays a large humidity-driven locomotion with an atypical fast unbending. Cationic exchange of the anionically charged TCNF-Na⁺ and control of the layer thickness is used to tune and dictate the locomotion and actuator’s response to humidity variations. Assembly of a self-oscillating electrical circuit, that includes a conductive rGO layer, displays autonomous on-and-off lighting in response to actuation-driven alternating electrical heating.

1. Introduction

Actuators are devices that can convert environmental stimuli such as light,[11] magnetic or electric field,[2] pH,[3] temperature,[4] electrochemical,[5] and moisture[6] to mechanical energy to drive physical motions. The interest in soft or hybrid actuators, where the actuators are built up entirely or partly from soft matters, respectively, is on a constant rise because of their potential applications in various areas such as environment-triggered sensors,[7] soft robots,[8] artificial muscles,[9] and controllable displays,[10] just to name a few. (Bio)synthetic soft actuators can be classified into two categories depending on the actuation mechanism. The one based on a molecular order change includes ferroelectric polymers, shape memory polymers, and liquid crystal elastomers (LCEs).[11] The latter has been widely investigated, for instance, as artificial muscles and smart photonic materials, since de Gennes et al. paved the way in 1997.[12] The other one is based on a volume change arising from an intrinsic structural inhomogeneity leading to an asymmetric absorption of solvent molecules, gas, or ions. Typical examples include hydrogels, swelling electroactive polymers, as well as films and fibers. Those soft actuators can be bilayer, trilayer, or gradient based.[13]

Bilayer actuators consist of one active and one less active or inert layer that respond differen tally to an external stimulus. The asymmetric stimulus-driven volume expansion of the two layers generates an internal stress at the interface that results in a physical movement or deformation. Humidity-based actuators[14] utilize the intrinsic sensitivity toward water vapor to induce and drive mechanical movement that follows and reflects the time-dependent change in humidity. In this regard, nanomaterials which benefit from a high aspect ratio of the surface area to volume are very suitable for the construction of sensitive and fast actuators, as the moisture sorption process by the actuator is kinetically surface controlled. Typical nanomaterials include 1D materials, for example, cellulose nanofibrils (CNFs), carbon nanotubes (CNTs), and the electrospun polymer nanofibers, as well as 2D materials, for example, graphene, graphene oxide (GO), and the carbide/nitride MXene family. They are excellent candidates as building blocks (either active or inert layer) for actuators. In literature, humidity-responsive nanostructured bilayer actuators composed of graphene oxide in combination with reduced graphene oxide (rGO) or CNTs have already been extensively studied.[16] Recently, humidity-responsive actuators built solely from CNFs or in combination with Ti₃C₂Tx MXene were reported.[16] Nevertheless, none of them are conductive due to the intrinsic insulating property of CNFs. A humidity-responsive hybrid nanostructured bilayer actuator composed of both CNFs and rGO nanomaterials might synergistically combine the moisture sensitivity of the CNF with the electron conductivity of rGO to realize new functions in actuating devices.

Here, we report a hybrid 1D/2D nanomaterials-based actuator composed of CNF and rGO. The hybrid actuator was fabricated by consecutive filtration-assisted deposition of two thin films from the aqueous CNF and GO dispersions on a porous support, followed by the reduction of GO into an electrically conductive rGO layer by hydrogen iodide (HI). The structure of the designed actuator was analyzed, optimized, and then its actuation

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DOI: 10.1002/aisy.202100084
performance was further evaluated. An unusually faster unbending than bending motion was remarked and identified to be related to the humidity-dependent swelling and deswelling of the CNF film. The actuation behavior was repeatable over at least 100 cycles and could be modulated either by the type of cations on the CNF surface or by the relative thickness of the CNF layer to the rGO layer. A self-oscillating lighting device in a humid air was constructed via the alliance of the bilayer’s actuator function and the conductive property of the rGO layer.

2. Results

2.1. Choice of Nanomaterials

CNF is a family of hygroscopic bionanofibrils with nanosized diameter and a length of up to tens of micrometers with a property profile greatly different from wood fibers \( (d \approx 30 \mu m) \).\[17\] This family of 1D biomaterials is typically water dispersible due to surface charge derived from its production process and possesses outstanding physicochemical properties that are governed by how well the fibrils are individualized. In that manner, \((2,2,6,6\text{-tetramethylpiperidin-1-yl)oxyl}} \) TEMPO, a room-temperature stable radical catalyst that can oxidize selectively the primary alcohols to aldehydes under mild conditions,\[18\] can be employed as chemical pretreatment during the synthesis of CNF. When TEMPO is combined with the oxidant sodium hypochlorite and a catalytic amount of NaBr, one obtains a regioselective conversion of C6 primary hydroxyls to carboxylate groups via aldehydes.\[19\] This chemical pretreatment can facilitate the complete disintegration of wood pulp fibers toward fully individualized nanofibrils, thanks to osmotic effect and/or electrostatic repulsion\[20\] \( (d < 5 \text{ nm}) \) to enhance their hydrophilicity.

TEMPO-oxidized CNF \( \text{(TCNF-Na}^+ \text{)} \), Figure S1a, Supporting Information) is chosen here to construct the hygroscopic active layer of the actuator on account of its favorable properties, that is, high stiffness and flexibility,\[21\] (ultra)high aspect ratio, light weight, hydrophilic and ionic surface, along with durability, that are highly desirable in humidity-sensitive actuator application. Their nanometer-scale lateral dimensions allow for facile bending and unbending.

Meanwhile, since its discovery, graphene\[22\] and its derivative such as reduced graphene oxide (rGO) have been widely investigated in the design of actuators.\[23\] Due to their atom-thick 2D structures, they possess remarkable properties such as low weight density, large surface area, high mechanical strength, chemical/thermal stability, nonswellability, and high electrical conductivity.\[24\] rGO is sometimes preferred to graphene because it can be synthesized at scale by solution-based processing methods.\[25\] Fully reduced GO is graphene like with high density of defects and some residual oxygen-containing groups. The sheet (flake) thickness of a single-layered rGO flake is subnanometer with lateral dimension as large as micrometers.\[25a\] In this work, HI vapor was used as GO reducing agent because HI has little-to-no impact on the mechanical performance of the resultant rGO film in comparison with other reducing agents.\[26\]

2.2. Fabrication of the Hybrid Bilayer Actuator

The fabrication procedure of the hybrid nanostructured actuator is shown in Figure 1. First, a 0.01 wt% aqueous CNF dispersion was vigorously shaken and sonicated for 2 min. A good dispersion is essential to preserve the optimal properties of CNFs during the processing procedure. Several well-defined volumes of this dispersion in the range of 9.38–88.48 mL were deposited
onto a porous poly(vinylidene fluoride) (PVDF) membrane support (pore size: 0.22 μm and membrane diameter: 4.7 cm) via a pressure-assisted filtration–deposition method. After 3 h, the first layer of the actuator was formed with entangled nanofibrils. While this layer was still wet (Figure S2, Supporting Information), 1.46 mL of a GO dispersion (2.4 mg mL⁻¹, Figure S1b, Supporting Information) was deposited onto the top of the CNF layer in the apparatus and vacuumed. The pressure filtration stacked the GO sheets parallel onto each other to form a densely packed film. Thereafter, the freshly formed bilayer was allowed to dry in the filtration device in air for 1 h at room temperature. Once peeled off, the bilayer film was exposed to HI vapor at 60 °C for 6 h to reduce the GO sheets, followed by washing with acetone to remove the residual HI and the formed I₂ substance. The nonprotic acetone was used here to prevent any potential cation exchange of the Na⁺ on CNF surface by H⁺. Six distinct bilayer actuators were generated in this way with varying CNF film thickness and a constant rGO set at 0.40 ± 0.04 μm. The rGO film serves as the inert layer and as a moisture barrier. The actuators are labeled “TCNF-Na⁺/rGO”, where y represents the thickness of the CNF layer. The value of “y” was determined by statistical analysis of their thickness through scanning electron microscopy (SEM) to be 0.12 ± 0.03, 0.37 ± 0.03, 1.31 ± 0.08, 2.28 ± 0.11, 3.01 ± 0.14, and 4.18 ± 0.16 μm for each constructed actuator (Figure S3a-f, Supporting Information). The bilayer was then cut into rectangular strips with a defined size of 5 mm × 1 mm.

2.3. Structural Characterization of the TCNF-Na⁺/rGO Bilayer Actuator

Atomic force microscopy (AFM) images of GO (Figure 2a) demonstrate the presence of single-layered flakes with an average sheet depth of ≈0.8 nm and a very diverse lateral size (Figure S4, Supporting Information). In addition, characteristic wrinkles formed due to the edges of GO sheets can be observed.

![Figure 2](image-url)
The presence of exfoliated GO flakes is further supported by transmission electron microscopy (TEM) and powder X-ray diffraction (PXRD) (Figure S5, Supporting Information). Similarly, the AFM images of TCNF-Na⁺ shown in Figure 2b depict individual nanofibrils, indicating that conversion of the fibril aggregates (≈30 nm in width)²⁰ within the fiber wall to totally liberated individual fibril elements²⁹ did occur. The separated nanofibrils possess an average diameter of 1.8 ± 0.6 nm, as determined from their AFM height profile. The morphology and cross section of a representative actuator (TCNF-Na⁺ 0.37 μm/rGO) can be visualized by SEM in Figure 2c, whereas its optical appearance is shown in Figure S6, Supporting Information. The adhesion between the CNF and adjacent rGO films is believed to originate from intermolecular interactions. Indeed, rGO has both some residual –OH and –COOH groups on its surface, and a re-established aromatic σ-system. Thus, in a semidry state, rGO can naturally interact with the negatively charged CNF (surface functionalized with COO⁻ groups) via H-bonding and anion–σ interaction (Figure S7, Supporting Information). The nature of the anion–σ interaction stems from the anion–dipole interaction, where the dipoles of the rGO are induced by its residue –OH/COOH groups and also the adjacent ions on the CNF surface.³⁰

The stress–strain curves of both the pristine TCNF-Na⁺ 0.37 μm film and the TCNF-Na⁺ 0.37 μm/rGO bilayer actuator are measured at ambient condition, namely, 21 °C and 25% relative humidity (RH), as shown in Figure 2d and Table S1, Supporting Information. As a reminder, RH is an indication of how much moisture is in the air versus how much water the air could hold at a given temperature. It can be measured by taking the ratio of the partial pressure of water vapor in a fixed environment and the pressure point at which water vapor saturates the air.³¹ Mechanical performance of the CNF films can vary drastically depending on various aspects such as the synthetic route, degree of polymerization (DP), moisture content, porosity, and alignment of nanofibrils.³² In this work, the vacuum-assisted filtration method for the film formation produces nanofibrils in the film with no positional order but with their long axes staying roughly in parallel to the film plane, in comparison with other techniques.³¹ The nanofibrils are highly charged as proven by ζ-potential measurement (−51 ± 1.6 mV, Figure S8, Supporting Information). A carboxylate content of 1.44 ± 0.06 mmol g⁻¹ was determined by the conductometric titration test (Figure S9, Supporting Information) and suggested that almost all of the C₆-primary hydroxyl groups exposed on the surfaces of the CNF were oxidized to C₆-carboxylates.³³ A high charge density has been reported to reduce the fiber length and in combination with extended sonication time can decrease the degree of polymerization of cellulose chains within the fibers.²⁹ A low degree of polymerization (DP) (shortening of cellulose chains) and a high RH will induce a decrease in mechanical performance. More specifically, for the latter, compared with films made up of cellulose microfibers, CNF films are much more sensitive to water vapor due to their hydrophilic high surface area and important swelling effect generated by the water uptake of the films.³⁵ In symbiosis, the charged carboxylate groups of the nanofibrils increase the water ingestion by an osmotic swelling pressure, opening the film network further for additional moisture uptake. Therefore, decrease in both strength and stiffness as well as an increase in ductility are observed in the CNF films at high RH.³²

As experimentally confirmed in this work, at 25% RH, the pristine TCNF-Na⁺ 0.37 μm film possesses excellent mechanical properties with an average Young’s modulus of 13.7 ± 0.9 GPa, tensile strength of 156.7 ± 10.1 MPa, and strain at break of 1.1 ± 0.1%. At this low–medium RH, the strength of the CNF film is larger than the standard synthetic films, that is, polyethylene and polypropylene.³³ The high stiffness and strength values are probably due to the numerous hydrogen bonds within the CNF. At 95% RH, one can remark a mechanical softening of the TCNF-Na⁺ 0.37 μm film as demonstrated by tensile testing with an average Young’s modulus and strength values dropping down to 561.2 ± 23.6 and 15.3 ± 3.3 MPa, together with a strain at break of 3.3 ± 0.4%, respectively. The source of this weakening is likely to stem from the hydrophilicity of the CNF film that promotes swelling, the loss of interfibrillar hydrogen bonding, and the increased interfibrillar slippage.³⁴,³⁶ Finally, under ambient condition, the bilayer actuator (TCNF-Na⁺ 0.37 μm/rGO) was shown to be more brittle than the pristine CNF film with a strain at break of 0.59 ± 0.07% alongside a weaker tensile strength of 58.6 ± 6.8 MPa and a toughness of 0.14 ± 0.09 MJ m⁻³, while keeping excellent stiffness with an average Young’s modulus of 8.8 ± 0.6 GPa.

2.4. Actuation Performance

The actuation performance can be evaluated by the maximum curvature (Figure S10, Supporting Information), the bending and unbending kinetics, and durability in repeated actuation cycles. The actuation of the bilayer based on CNF and rGO originates from the asymmetric volume expansion of the active CNF layer that is attached to the inert rGO layer. The CNF layer will expand and swell when exposed to an increased RH due to water vapor uptake. In contrast, the rGO layer is less sensitive to moisture because of its high surface hydrophobicity and compact packing. This difference in affinity to water between the hygroscopic CNF and the hydrophobic rGO layers results in bending when the laminated actuators are exposed to air of a higher humidity. Out of the six constructed actuators, the TCNF-Na⁺ 0.37 μm/rGO was the fastest and yielded a response time of 23.5 s when the RH was increased from 25% RH to 95% RH (Figure 3b), with a maximum curvature of 1.57 mm⁻¹ (Figure 3a). The TCNF-Na⁺ 0.37 μm/rGO actuator closes one complete cycle (bending angle: 360°) in ≈8.8 s on average. When the RH was decreased from 95% RH to 25% RH, the TCNF-Na⁺ 0.37 μm/rGO bilayer actuator recovered a zero curvature in ≈0.92 s (Figure 3b, Movie S1 and S2, Supporting Information). The actuation behavior was found to depend on the thickness of the active layer (the thickness of the rGO layer is fixed). For the actuator with the thinnest CNF layer (TCNF-Na⁺ 0.12 μm/rGO), essentially no actuation was observed. The fastest actuation motion combined with the maximum bending curvature was obtained for the TCNF-Na⁺ 0.37 μm/rGO actuator, whereas the actuation behavior (curvature and kinetics) was less pronounced and slower for actuators with a growing TCNF-Na⁺ layer thickness (Figure S11, Movie S1 and S2, Supporting Information). Indeed, due to the water uptake, the swelling-
induced force exerted by the CNF layer at the interface with the rGO layer is expected to increase with the thickness of the CNF layer but the intrinsic stiffness of CNF films is believed to result in a rising resistance to bending with thickness enlargement.

The reference state, that is, the point defined as curvature 0 (where the actuator is flat), was experimentally observed to occur at 80% RH. Gradually, the curvature grows to reach a maximum of 1.57 mm⁻¹ at 95% RH, passing by values of 0.314 mm⁻¹ at 87% RH and 0.942 mm⁻¹ at 92% RH in the process (Figure 3c). The curvature and actuation rate of the TCNF-Na⁺₀.₃₇µm/rGO actuator were further investigated by cycling between 25% and 95% RH, as shown in Figure 3d. The actuator exhibited reversible and repeatable bending and resulted in a minor curvature loss of ≈10%, along with a slightly slower response time after 100 cycles (Figure 3d, Movie S3, Supporting Information). The minor loss of actuation performance could probably be ascribed to an increase in the water content that remained in the actuator at the lowest RH with repeated cycling. Indeed, the actuation performance could be restored by placing the actuator first in a vacuum chamber (0.01 mbar) for 1 h at room temperature and then in air under ambient conditions. This treatment recovers the same maximum curvature and kinetic as measured in the initial cycles. It is worth noting that the actuator goes beyond the reference (flat) state in the process of going from a 95% RH environment to 25% RH (Movie S1 and S2, Supporting Information) and that a negative curvature is therefore observed. This negative curvature is stochastic. Its bending angle and direction are random in contrast to how it behaves at high RH, where one can determine its curvature, kinetic, and direction accurately. This phenomenon is probably due to a relaxation process caused by the stresses generated by the bent state at 95% RH and the very fast water desorption.

A plot of “maximum curvature” versus time is used to compare the performance of the designed actuator with other humidity-driven soft actuators in terms of the maximum
curvature attained and how fast to reach it. From Figure S12a, Supporting Information, one can observe that TCNF-Na$^+$ \(_{0.37 \mu m}/rGO\) is in the typical response time range of humidity-sensitive actuators (from 0.4 to \(\approx 125\) s) and holds the highest bending curvature. Figure S12b, Supporting Information, allows to clearly highlight the engineered actuator in terms of its extremely fast unbending motion, where the unbending response time is, to the best of our knowledge, the quickest among all humidity-driven bilayer actuators by far.

2.5. Actuation Mechanism of the TCNF-Na$^+$/rGO Bilayer Actuator

In previous studies, the pore size of the TCNF-Na$^+$ film was determined experimentally at 0% RH to be \(\approx 5\) Å.\(^{[17]}\) The porous structure within the CNF layer (Figure S13, Supporting Information) promotes the uptake and removal of water with changes in the RH in the surrounding air. The volume increase, that is, swelling of CNF films, is mainly related to the penetration and sorption of water molecules between the individual nanofibrils and, to a lesser extent, because of the expansion of the nanofibrils.\(^{[38]}\) However, the partly amorphous CNF may display a larger intrinsic water uptake and expansion than highly crystalline nanocellulose materials such as cellulose nanocrystals (CNCs).\(^{[39]}\) The adsorption of water onto the fibril surface can be tuned and controlled by, for example, the surface charge density of the fibrils; the more charged it is, the higher the water adsorption capacity is expected to be.

The moisture sorption and swelling rate depend on the transport and diffusion of water into the fibrillary network and the adsorption of water molecules to accessible surface sites possessing hydroxyl and carboxylate groups through H-bonding interaction and sorption of water by the less-accessible sites and internal amorphous moieties as the films swell.\(^{[40]}\) Water can also condense in small pores. The resulting swelling of the active layer can be impeded when the volume expansion of a hydrated nanofibril is physically hindered by the interpenetrated nanofibril network.\(^{[41]}\)

Measurements of the moisture uptake by the CNF films show that there is a 39% increase of the moisture content when changing the RH from 25% RH to 80% RH (Figure S14, Supporting Information). The water uptake results in swelling of the film and an increased film thickness by 3 \(\mu m\). Further increase in the RH from 80% to 90% leads to an increased moisture content of 13%, whereas the thickness of the film remained roughly the same. It should be pointed out that it is difficult to accurately determine the thickness of highly swollen and soft CNF films, which may explain the relatively high standard deviation.\(^{[42]}\) The desorption that follows the lowering of the RH back to 80% corresponds to 11% decrease in the moisture content and an approximate decrease of the film thickness by 2 \(\mu m\). Reducing the RH from 80% to 25% leads to a decrease in the moisture content of 43% and an approximate thickness shrinkage of 3 \(\mu m\). This indicates that the water adsorption and desorption of the films are reversible processes.

Now, based on the Timoshenko theory,\(^{[43]}\) the bending curvature (\(\kappa\)) can be simplified as in Equation (1).\(^{[44]}\)

\[
\kappa \sim \frac{1}{h}(e_s - e_i)
\]

where \(h\) is the bilayer actuator thickness and \(e_s\) and \(e_i\) are the swelling strains by water adsorption on the active and inert layers. The noninfiltration of water molecules from the rGO layer side creates a large imbalance of water adsorption between the two layers. This gives rise to the anisotropic swelling across the bilayer actuator, which brings a larger strain difference between the active and the inert layer, \(e_s >> e_i\), yielding a high curvature. To note, even if the rGO layer would allow for water penetration, the hybrid bilayer would still actuate, as the rGO layer in fact does not swell.

The peculiarity of the designed actuator is that in all curvature kinetics measurements (Figure S11, Supporting Information), the unbending (= desorption of water molecules, deswelling) is much faster than the bending (= water uptake and swelling). This behavior is different from common humidity-sensitive bilayer actuators reported in literature, where the bending (\(\Delta RH > 0\)) actuation is faster than the unbending (\(\Delta RH < 0\)). Both low and high RH settings can be approximated as containing an infinite air volume as the volumes are, respectively, a laboratory room and a 900 mm \(\times 500\) mm \(\times 500\) mm humidity box with no humid air forced to circulate. Therefore, the difference in time response is not a trivial reflection of the different experimental settings. In contrast, a hypothesis for the origin of this fast unbending behavior might be the observed softening of the CNF layer at a high RH due to the well-known water uptake-induced swelling of the CNF layer.\(^{[32]}\) As the force is similar, the desorption speed is much faster as the mechanical resistance of the CNF layer with a high swelling degree becomes substantially lower than the original strong and drier actuator (at 25% RH). Hence, unbending is considerably quicker than bending.

2.6. Cation Exchange Control of the Actuation Performance

Further study of the hybrid bilayer actuator was given to the cation effect (Figure 4). Based on the optimized actuator TCNF-Na$^+$ \(_{0.37 \mu m}/rGO\), we exchanged the sodium counter-cation of the nanofibrils by H$^+$ and three tetraalkylammonium cations, namely, tetraethylammonium (TEA$^+$), tetrabutylammonium (TBA$^+$), and tetrahexylammonium (THA$^+$) (Figure S15, Supporting Information). The success of the cation exchange was proven by attenuated total reflectance–Fourier-transform infrared (ATR–FTIR) measurements (Figure S16, Supporting Information). The initial postulate is that by introducing quaternary ammonium cations with an increasing hydrophobic alkyl tail, the ion pair would become progressively more hydrophobic, thus reducing interaction with moisture. The aim of this postulate is to control the actuation behavior of TCNF-X$^+ \_ {0.37 \mu m}/rGO$ (where X$^+$ = Na$^+$, H$^+$, TEA$^+$, TBA$^+$, and THA$^+$). Indeed, the actuation performance followed the order Na$^+$ > H$^+$ > TEA$^+$ > TBA$^+$ \(\approx\) THA$^+$ for the cation-exchanged actuators (Figure 4a). The strong “TCNF-Na$^+$–water” and “TCNF-H$^+$–water” interactions yielded better performance than the actuators with quaternary ammonium cations due to the weaker “TCNF-tetraalkylammonium–water” interaction. As expected, with the increased hydrophobic alkyl tail of the
quaternary ammonium cation, the corresponding maximum curvature kinetics decreased from 0.53 mm⁻¹ to 0.19 mm⁻¹ (Figure 4b, Movie S4 and S5, Supporting Information). Presumably, the bulky quaternary ammoniums as counter-cations for the carboxylate anions on the nanofibril surface impedes the formation of hydrogen bonds. To note, the TCNF-H⁺₀.₃₇μm/rGO actuator has a lower curvature than the TCNF-Na⁺₀.₃₇μm/rGO one, as not all H⁺ will be dissociated from the carboxylate anion in a wet condition.

2.7. Application of the Hybrid Actuator in an Autonomous On-and-Off Lighting Device

Taking the advantage of the electron conductivity of rGO, a self-oscillating electrical circuit composed of the TCNF-Na⁺₀.₃₇μm/rGO actuator serving as a switch was designed (Figure 5a, Figure S17, Supporting Information). When exposed to a high RH (92%), the actuator bent to connect an electrical circuit to switch on a lamp (Movie S6, Supporting Information). Then, the current ran through the entire circuit. Due to the heat generated locally on the rGO film by the current, water evaporated partially from the CNF layer. This is sufficient for the actuator to unbend in that process detaching the contact and turn off the lamp. This is the first on-and-off cycle. The actuator still stayed exposed to the high RH environment, and soon after the cooling down of the rGO layer, the CNF layer would swell enough again by moisture, leading to re-bending of the actuator that further connects the electrical circuit to light up the lamp. It was then followed by generation of heat caused by electricity on the rGO layer to once more desorb moisture and unbend the actuator to disconnect the circuit. This repeated bending and unbending cycle builds up an autonomous self-oscillating system, as shown in Figure 5b, where the on/off state of the actuator-based circuit against time is plotted.

3. Conclusion

We demonstrate that a hybrid bilayer nanostructured actuator made from a TCNF-Na⁺ film and rGO film allows for water vapor-controlled actuation that is sensitive to variations of humidity levels in air. The TCNF-Na⁺ active layer has a large capacity to sorb water that was related to the highly hydrophilic nature of nanocellulose and the microporous structure of the deposited film. The actuation of the hybrid bilayer is reversible with good stability and durability. The designed actuator can be easily scaled up into a large size. The extent of bending of the
actuator can be controlled by either the active layer thickness or by the types of counter-cations. Moreover, all used nanostructured materials, here CNF and rGO, are accessible and also commercially available. The hybrid actuator can be used as a humidity-based sensor or switch. We showcase a humidity-controlled on-and-off lighting device that is enabled by the bending and unbending of the actuator that contains a conductive rGO layer.

4. Experimental Section

**Chemicals and Materials:** A never-dried sulfite softwood-dissolving pulp (moisture content: 60 wt%) was provided by Domsjö Fabriker AB (Ornsköldsvik mill, Sweden). This pulp source is known for its high-purity cellulose from softwood fibers (Norwegian spruce) with a high cellulose content in the dry state (95% cellulose, 4.5% hemicellulose, and 0.1% lignin content).\(^{(20)}\) Graphite powder (325 mesh) was obtained from Tsinghua University (Beijing, China). Sodium hypochlorite (available chlorine: 11–15%) and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO ≥ 98%) were purchased from Alfa Aesar. Potassium permanganate, ethanol (95%), and hydrogen iodide (57%) were purchased from VWR International Ltd. and hydrogen iodide (57%) was purchased from Sigma-Aldrich. Sulfuric acid (95%) and sodium hydroxide (≥99.2%) were purchased from WWR International Ltd. and hydrogen iodide (57%) was purchased from Fisher chemical. All the chemicals were of analytical grade without further purification. Deionized (DI) water was used in all experiments.

**Synthesis of High-Charge (1.44 ± 0.06 mmol g⁻¹ Carboxylate Content)**

**Tempo-Oxidized CNFs:** The synthesis was based on a procedure by Saito et al. under alkaline conditions.\(^{(20)}\) Never-dried pulp was prewashed with DI water by vacuum filtration (20 µm nylon membrane). The prewashed pulp was dispersed with a mechanical stirrer in water for 15 min and then pH was adjusted to ≈2.5 using 0.1 M HCl solution and vigorous stirring proceeded for another 15 min. Washing with DI water via vacuum filtration was conducted afterward until neutral pH. 1 wt% of washed pulp (45 g dry weight) was dispersed in water for 1 h and then 0.72 g TEMPO was added until it fully dissolved, followed by addition of 4.5 g NaBr. Oxidization was triggered when 10 mmol g⁻¹ of NaClO solution (13.93% available chlorine, 199.4 mL) was carefully added drop wise (to always stay below pH 10) to the mixture (turned yellow) under constant mechanical stirring. Then, oxidation proceeded for 4 h and pH was constantly adjusted to 10 through stepwise addition of 0.3 M NaOH. The reaction was quenched by ethanol (≈75 mL) and the oxidized pulp was thereafter filtered off by vacuum filtration with DI water until it was neutral pH. The oxidized pulp was hereafter dispersed in DI water to a 1 wt% concentration with vigorous stirring for 1 h and the pH was increased to 10. Addition of 4.5 g NaBH₄ followed to reduce the residual aldehydes that did not get oxidized completely to carboxylate groups\(^{(26,46)}\) into primary alcohols for 3 h. Final washing of the pulp by vacuum filtration was conducted until it was neutral pH. A ≈1 wt% dispersion was set up under vigorous stirring to allow the fibers to swell (to facilitate the liberation of the fibrils). Immediately followed by mechanical disintegration of the high-pressure homogenizer APV 2000 (Spixell, USA), in a sequence consisting of two passes at a pressure of 500 bar to obtain a highly viscous 7.0 wt% TCNF-Na⁺ hydrogel.

**Synthesis of Graphene Oxide:** GO was prepared by the conventional Hummer’s method. Graphite powder (325 mesh, 1.5 g) was slowly added into 95% H₂SO₄ (35 mL) in a beaker under constant stirring at room temperature. Following addition of sodium nitrate (0.75 g), the reaction slurry was vigorously stirred at 0 °C (ice bath), whereas potassium permanganate (4.5 g) was slowly added for over 10 min. Thereafter, the reaction mixture was transferred to a 35 °C water bath where the oxidation reaction continued for more than 0.5 h under constant stirring to form a thick paste. Subsequently, DI water (70 mL) was poured into the mixture and stirring continued for another 15 min at 95 °C. Additional DI water (250 mL) was added to the mixture followed by slow addition of H₂O₂ (30%) to reduce Mn (VII) species until no bubbles were observed (color of the solution went from brown to yellow). The obtained GO was filtered and washed with at least 1000 mL aqueous HCl solution (v/v = 1/10 from 37% concentrated aqueous HCl solution and DI water) for three cycles to remove any residual acid via centrifugation (10 000 rpm for 1 h in each cycle). The resulting solid was then dispersed in DI water under mild sonication at 20 °C for 10 min. The obtained GO dispersion was purified by dialysis for 2 weeks and then three cycles of centrifugation (2000 rpm for 30 min in each cycle) followed to remove any residual metal ions, graphite powder, and unexfoliated GO agglomerates. Finally, the pure dilute GO aqueous dispersion was concentrated by centrifugation at 10 000 rpm for 1 h to form the GO stock.

**Preparation of TCNF-Na⁺/rGO Bilayer Membrane Actuators:** A 0.01 wt% TCNF-Na⁺ dispersion was shaken and sonicated for 2 min. Different volumes (9.38, 17.08, 35.70, 53.20, 72.1, and 88.46 mL) were poured onto the porous PVDF membrane (pore size: 0.22 µm support and filtered into films via a pressure-assisted filtration–deposition method. Subsequently, GO dispersion (2.5 mg mL⁻¹) was deposited onto the first layer and vacuum filtered to get a bilayer film. Note that the PVDF membrane pore size was small enough to block the passage of GO with a lateral size greater than 0.22 µm and all TCNF-Na⁺ nanofibrils. The bilayer film was readily peeled off from the PVDF filter support membrane after drying in open air for 1 h. The reduction of the GO layer was conducted in a Hi atmospheric environment at 60 °C for 6 h. Then, the bilayer film was washed for 12 h by acetone to remove any residual I₃⁻ molecules adsorbed on the actuator. The aprotic organic solvent acetone was chosen wisely to avoid cation exchange from Na⁺ to H⁺ in the TCNF-Na⁺ layer.

**H₂O Sorption/Desorption Measurements:** The moisture sorption and desorption of a representative CNF film of 4.18 µm in thickness were evaluated gravimetrically.\(^{(47)}\) The water sorption was expressed as the H₂Oₛ (wt%) at a selected RH. The CNF film was placed in a well-ventilated...
plastic container inside a humidity chamber. The mass was measured continuously every 5 min using a high-precision balance (BP 210 S, Sartorius, Germany). The CNF films were conditioned at 313 K and 20% RH before the adsorption measurements were carried out at 295 K and 25%, 80%, as well as 90% RH. This was followed by the desorption measurements going down from 90% to 80% and 25% RH. The sample was held at the desired RH for at least 6 h to ensure a steady state. When the desired RH was reached, the film thickness was determined at three points using a digital caliper (Schut Geometrical Metrology electronic outside micrometer, EU). An attempt to reach 95% RH was conducted but troublesome due to condensation issues and thus was not evaluated. The measurements were carried out twice, according to the sequences 25–20–25–25% RH and 25–20–90–25% RH, respectively.

**Cation Exchange:** Once the TCNF-Na\(^+\) layer was formed, a 0.01 M HCl solution (50 mL) was poured on top of the layer and vacuumed until all solution went through the CNF film. Washing with DI water (≈ 200 mL) was conducted to remove free H\(^+\). Three quaternary ammonium hydroxides were employed in the cation-exchanged treatment of TCNF-H\(^+\). A 0.4% aqueous solution of each quaternary ammonium hydroxide in water (30 mL, dry weight ≈ 120 mg) containing excessive molar amounts of cations than H\(^+\) in TCNF-H\(^+\) was injected in the vacuum-assisted filtration device. The rest of the bilayer fabrication procedure was conducted as previously described to deposit the GO layer and reduce it.

**Characterization:** FTIR spectroscopy data were collected on a Varian 670-IR spectrometer (Varian, USA) using a single reflection diamond ATR accessory and a room-temperature detector. Background and sample total scan were set to 32 each.

PKRD was conducted on a powder diffractometer Panalytical X’Pert pro (Malvern Panalytical, UK) utilizing nonmonochromatic Cu K\(_\alpha\) radiation. An accelerating voltage of 40 kV, current of 40 mA, step size of 0.0167°, and scan speed of 0.0235° s\(^{-1}\) were used for each analysis and data were collected from a 2\(\theta\) range starting from 4° up to 80°.

SEM was conducted in a field-emission JEM-7000 F (JEOL, Japan). Signals from the SE detector were used for image formation. Samples were placed on a carbon conductive tape and imaged at varying accelerating voltages (1, 5, and 10 kV). SEM images analyses were conducted on the ImageJ 1.45s software (NIH, USA).

TEM images were conducted on a JEOL JEM 2100 LaB\(_6\) (JEOL, Japan) operating at 200 kV. GO sample was drop cast on a continuous carbon-coated Cu grid.

APM topography images of the nanomaterials were conducted on a Multimode AFM Nanoscope V (Veeco Instruments, USA). The AFM metal disc was glued, and freshly cleaved mica surface was put on top of it. TCNF-Na\(^+\) and GO suspensions were diluted down to 0.0001 wt%. For each measurement, 300 µL of the dispersion was deposited on a mica substrate and dried for at least 12 h in air. For GO sample, APM images (height, amplitude, and phases) were acquired continuously in the tapping mode under ambient conditions using standard TESPAMV2 silicon nitride probes (Bruker, USA) with spring constant \(k = 40 \text{ N m}^{-1}\) and tip radius of 8 nm (according to the manufacturer’s specifications). For TCNF-Na\(^+\) sample, APM images (height, amplitude, and phases) were acquired using the probe ScanAsyst-air (Bruker, USA) with spring constant \(k = 0.4 \text{ N m}^{-1}\) and tip radius of 2 nm (according to the manufacturer’s specifications) under Peak Force tapping mode. The collected data were processed with the software NanoScope Analysis 1.5 (Bruker, USA). Height images of TCNF-Na\(^+\) were subjected to third-order polynomial flattening.

**Mechanical Tests:** Tensile properties of the materials were examined on an Instron 5960 universal testing machine (Instron, USA) with a 100 N load cell and were strained at a rate of 10 mm min\(^{-1}\). All samples were kept at 23 °C and 50% RH for at least 24 h prior to measurement. Samples were cut with a razor blade into rectangular strips (width: 3 mm, length: 30 mm) and were clamped to the machine with a gauge length of 10 mm. The dry thickness of each sample was determined by cross-sectional SEM measurements. At least four independent measurements per sample were tested and the average Young’s modulus, strain at break, tensile strength, and work of fracture were calculated.

\[ \zeta - \text{Potential: } \zeta \text{-potential of TCNF-Na}^+ \text{ and GO (concentration 0.05 wt% each in milli-Q water, pH } = 7) \text{ was measured using a zeta sizer nanos ZS instrument (Malvern, UK) at 25 °C. Three measurements for each sample were carried out consisting of at least 50 runs per measurement with a duration of 10 s.} \]

**Water Vapor Stimulus Actuation:** The bilayer actuator was cut using a razor blade in rectangular strips (5 mm × 1 mm). The experimental settings were kept similar for each test. Namely, all actuators were placed inside a Torun glove box VGB-2 (Jiangsu, China) with an automatic humidity controller (1–99% RH). This glove box served as a large humidity box (900 mm length × 500 mm width × 500 mm height), where the temperature and RH were kept constant at 21 °C and 95%. The water vapor triggered the fast bending movement (Note: The reason why the actuation performance at high humidity was conducted at 95% RH and not 100% RH was because of the difficulty to control water vapor above 95% RH). The humidity box was very large with “infinite” air volume compared with the actuator dimensions and no humid air was forced to circulate. Afterward, the bilayer actuator was pulled back into laboratory room environment (25% RH and < 21 °C) to accomplish the shape recovery. Curvature was calculated at the maximum bending point of the bilayer actuator based on the formula \( k = r \theta / L \), where \( r \) is the radius of the bending loop. Response time was defined as the time taken from zero curvature to maximum bending angle of the actuator inside the humidity box, and the reverse process defined the recovery time. Reversible actuation performance was tested by recording 100 repeated cycles of water vapor stimulus actuation from 95% RH to 25% RH back and forth. All the actuation movements were recorded on either a smartphone camera or a high-speed camera Chronos 1.4 (krontech, USA) with extra lighting power delivered by a Godox SL-100 W LED light (Shenzhen, China), and the collected data were analyzed using the video editing software Premiere Pro (Adobe, USA).

**Curvature Measurements:** To measure the curvature, a rectangular strip of the actuator with one end fixed by tweezers was introduced inside a humidity box (95% RH). Curvature was calculated using Equation (2).

\[ k = \frac{\theta}{180 L} \text{ cm} \]

where \( k \) is the curvature, \( \theta \) is the central angle, and \( L \) is the film-free bending length.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

J. Y. is grateful for financial support from European Research Council (ERC) Starting Grant NAPOLI-639720, Swedish Research Council Grant 2018-05351, Dozentenpreis 15126 from Verband der Chemischen Industrie e.V. (VCI) in Germany, the Wallenberg Academy Fellow program (grant KAW 2017.0166) in Sweden, and the Stockholm University Strategic Industrie e.V. (VCI) in Germany, the Wallenberg Academy Fellow program (grant KAW 2017.0166) in Sweden, and the Stockholm University Strategic Indus.

**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.
Keywords

bilateral actuators, cellulose nanofibrils, humidity sensors, reduced graphene oxide, smart materials

Received: May 1, 2021
Revised: July 6, 2021
Published online: September 27, 2021
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