

Wet-Spun Stimuli-Responsive Composite Fibers with Tunable Electrical Conductivity

Anton Grigoryev, Vijoya Sa, Venkateshwarlu Gopishetty, Ihor Tokarev,
Konstantin G. Kornev,* and Sergiy Minko*

Wet-spun stimuli-responsive composite fibers made of covalently crosslinked alginate with a high concentration of single-walled carbon nanotubes (SWCNTs) are electroconductive and sensitive to humidity, pH, and ionic strength, due to pH-tunable water absorbing properties of the covalently crosslinked alginate. The conductivity depends on the material swelling in humid atmosphere and aqueous solutions: the greater the swelling, the smaller is the electrical conductivity. The covalently crosslinked fibers reversibly deform during the swelling/shrinking. In the swollen state, the fibers are less conductive, while they return to the same level of conductivity after shrinking. This unique reversible change of electroconductivity of the SWCNT-alginate fibers is due to the elastic deformation of the alginate network in the area of electrical contacts between SWCNT bundles arrested in the alginate matrix. Fibers of this kind can be used as a simple, robust, disposable, and biocompatible platform for electrotexiles, biosensors, and flexible electronics in biomedical and biotechnological applications.

1. Introduction

Only a few different examples of polymer-carbon nanotube (CNT) fibers have been reported in literature. These composite fibers were prepared by melt-spinning (with about 5 wt% of nanotubes in the dope),^[1] or wet-spinning from aqueous solutions (a much greater than 5 wt% nanotube concentration has been approached).^[2–4] The solution-spun fibers approach almost metallic conductivity, which makes them attractive for a number of applications including flexible electronics and sensors.^[5] The further development in the field of CNT-based fibers led to the discovery of a series of spinnable water-born compositions and wet-spun fibers for bioengineering applications.^[6,7] A polyelectrolyte hydrogel appears to be the most attractive matrix in the latter case.^[5]

Polyelectrolyte hydrogels offer a unique combination of biocompatibility and high water absorbency.^[8] The most attractive feature of polyelectrolyte hydrogels is that they are responsive to different stimuli: for example, the degree of swelling of hydrogels in aqueous solutions can be altered by changes in pH, salt concentration, temperature, or by additions of ligands, biomolecules, etc.^[9] The polyelectrolyte hydrogels fibers have a great potential for numerous biomedical and biotechnological applications.^[10] However, a combination of stimuli-responsive hydrogel fibers with conductive properties of CNT has not been yet demonstrated.

In this paper, we report on successful spinning and covalent crosslinking of alginate fibers loaded with a high concentration of single-walled carbon nanotubes (SWCNTs). These fibers demonstrate unique tunable water absorbing and elec-

troconductive properties, enabling conductometric monitoring of changes of the solution pH and controlling uptake and release of water. Advantages of this platform include material flexibility, stability in aqueous environment, and the ease of fabrication, which, along with material's responsiveness and biocompatibility of the alginate matrix, make it a great candidate for low-cost disposable and multiple-use sensing devices.

Alginate is a natural polysaccharide composed of two hexoses, guluronate and mannuronate, which contain carboxylic groups.^[11] The sodium salt form of alginate (sodium alginate) is well soluble in water due to dissociation of sodium carboxylate groups. Typically, alginate materials are ionically crosslinked in aqueous solutions containing divalent calcium ions to form a physical hydrogel.^[6c,10c] As a weak polyelectrolyte, the alginate hydrogel can alter its swelling degree with changes in the ionic strength of aqueous solutions of monovalent salts. Furthermore, by changing the solution pH, it is possible to reversibly switch alginate materials between the swollen and shrunken states.^[12] This transition is due to pH-dependent dissociation of a fraction of carboxylic groups, which are not bound by Ca^{2+} -ions, and reveals itself through changes in the swelling degree of the ionically crosslinked alginate hydrogel. The Ca^{2+} -crosslinked hydrogel disintegrates at $\text{pH} > 7$ and in the presence of monovalent cations, such as Na^+ , K^+ , and so forth,^[12b] due to ion exchange and “de-crosslinking”. The swelling degree of the alginate network is limited because of the involvement of a high fraction of carboxyl groups in the formation of the ionic crosslinks.

A. Grigoriev, Dr. V. Gopishetty, Dr. I. Tokarev,
Prof. S. Minko
Department of Chemistry and Biomolecular Science
Clarkson University
Potsdam, NY 13699, USA
E-mail: sminko@clarkson.edu
V. Sa, Prof. K. G. Kornev
School of Materials Science and Engineering
Clemson University
Clemson, SC 29634, USA
E-mail: kkornev@clemson.edu



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An ion-crosslinked alginate hydrogels at a high concentration of electroconductive fillers such as SWCNT almost lose their swelling behavior. Thus, this kind of ionically crosslinked fibers possesses no stimuli-responsive electroconductive and swelling properties. In this work, the replacement of ionic crosslinks by covalent crosslinks in the composite fibers revealed unexpected opportunities to combine pH- and humidity-responsive properties of the alginate hydrogel with tunable electrical conductivity of the fibers.

2. Results and Discussion

2.1. Synthesis of the Covalently Crosslinked Fibers

Alginate-SWCNT fibers were wet-spun using the method presented in the literature (Figure 1).^[6c] The dope was prepared by mixing a SWCNT dispersion with an aqueous solution of sodium alginate as described elsewhere.^[6c,13] The dispersion was injected through a needle into an aqueous calcium chloride coagulation bath, resulting in the ionic crosslinking of alginate by divalent Ca^{2+} ions and leading to the immediate gelation of alginate in the fiber form.

The Ca^{2+} -crosslinked fibers are unstable in basic solutions ($\text{pH} > 7$) and aqueous solutions of monovalent salts: the ion exchange between calcium ions in the fibers and

monovalent cations in solutions resulted in disintegration of the fibers. In order to make the fiber stable in aqueous solutions, the fibers were covalently crosslinked using glutaraldehyde chemistry,^[14] the second step in Figure 1b. To this end, dry calcium alginate composite fibers were treated by a water–acetone mixture with the added crosslinker. The covalent crosslinks were formed through the reaction of the carbonyl groups of glutaraldehyde with the hydroxyl groups of hexoses yielding the hemiacetal and then acetal groups. The crosslinked fibers were washed multiple times in large volumes of a 0.1 M solution of hydrochloric acid to ion-exchange calcium counter-ions of carboxylate groups with protons, resulting in the formation of $-\text{COOH}$ groups. Fourier transform infrared (FTIR) spectroscopy (Figure 1c) of the covalently crosslinked alginate confirms the formation of acetal groups and ion exchange of calcium counter-ions of carboxylate groups with protons.

2.2. Characterization of Size, Shape, and Swelling of Fibers

The proposed wet-spinning method allows for continuous formation of the alginate-SWCNT fibers. Specifically, a 1 to 1.5 meter-long fibers can be drawn out from the coagulation bath and wound on a Teflon rod. The drawn fibers were cut into smaller pieces for all experiments. At the spinning conditions

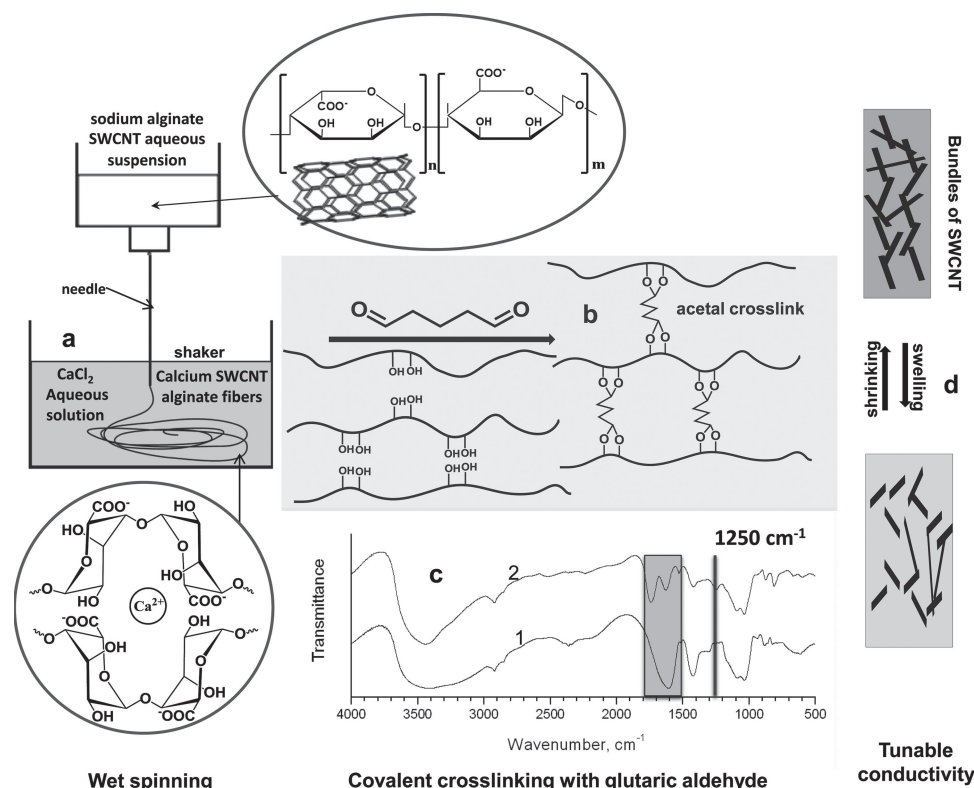


Figure 1. Different steps of the fabrication of alginate-SWCNT fibers: a) wet spinning of sodium alginate and a SWCNT dope in a CaCl_2 aqueous solution results in the formation of Ca^{2+} -crosslinked alginate-SWCNT fibers; b) covalent crosslinking of alginate with glutaraldehyde that is detected through c) a characteristic acetal band at 1250 cm^{-1} , and the formation of carboxylic acid groups at $1500\text{--}1800\text{ cm}^{-1}$ after ion exchange between calcium ions and protons as seen on the FTIR spectrum of 2) the acetal crosslinked fibers as compared with 1) the Ca^{2+} -crosslinked fibers; and d) schematic of a fiber undergoing the swelling-shrinking cycles upon changes in humidity, pH, or ionic strength.

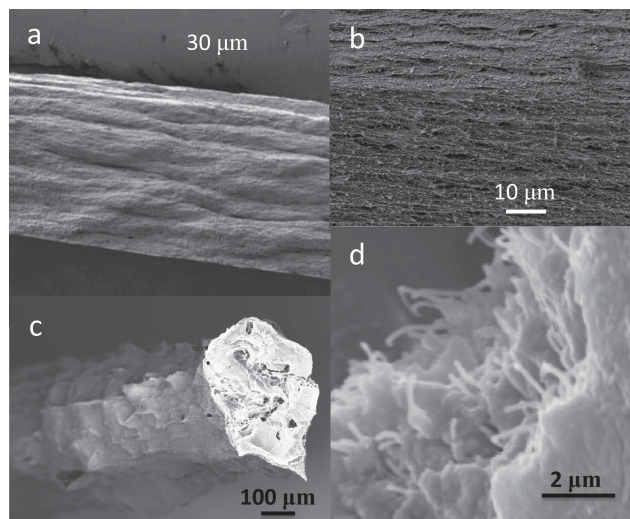


Figure 2. a–c) SEM images of the composite fibers with circular cross-sections at different magnifications that reveal d) SWCNT bundles at the locus of the fiber break.

of our experiments, the cross-section of the wet-spun fibers is circular as shown in scanning electron microscopy (SEM) images (Figure 2).

The resulting nanotube-loaded fibers, containing, for example, 12 wt% of SWCNTs, demonstrated a low electrical resistance, $3.7 \times 10^{-2} \Omega \text{ m}$ (conductivity of 2.7 S m^{-1}), and an about similar Young's modulus (1.45 GPa) as the alginate fibers without nanotubes.^[6c] The fragments of SWNT can be seen on the SEM image in Figure 2d, showing the fiber tip. The observed fibrous structures sticking out from the fiber tip likely represent about 100-nm-in-diameter alginate-decorated bundles of the 1-nm-in-diameter SWNTs. The electrical conductivity of the composite fibers originates from a SWCNT network where the electrical resistance is dominated by the inter-tube and inter-bundle contact resistances and the concentration of the bundles in the composites.

The covalently crosslinked alginate-SWCNT fibers remain stable in water in a broad range of pH and ionic strength values. Remarkably, these fibers swell in water to a much higher degree as compared to the Ca^{2+} -crosslinked counterparts before breakup (Figure 3). Swelling kinetics is also fast (on a timescale of seconds, Figure 4a). An enhancement of water absorption and fiber swelling can be rationalized as follows. In the ionically crosslinked alginate fiber, most of the carboxylate groups of alginate are in the form of an insoluble polyelectrolyte complex with calcium ions. In this case, the swelling of the material is driven by non-charged hydroxyl groups of alginate. Furthermore, it is important to note that the mannuronate hexose monomer units of alginate segregate into compact calcium “egg-box” domains.^[15] These domains are difficult to deform. Assuming that the egg-box domains behave as rigid spheres in an incompressible polymer matrix, the shear modulus of the weakly crosslinked material is estimated using the Dewey equation:^[16] $\mu = \mu_p(1 + (5/2)\phi)$, where μ_p is the shear modulus of the polymer without egg-box domains, and ϕ is the volume fraction of the egg-box domains. Therefore, the alginate network with

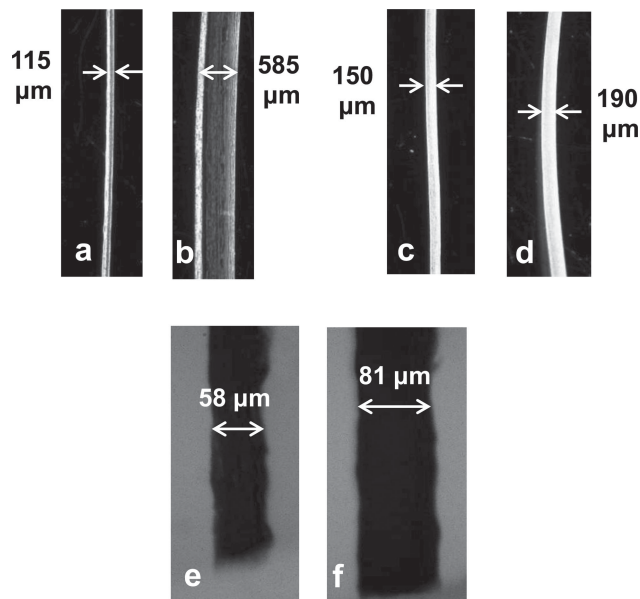


Figure 3. Optical images of the fiber samples (all the fibers have circular cross-sections): a,b) covalently crosslinked, c,d) Ca^{2+} -crosslinked, and e,f) SWCNT-loaded and a,c,e) covalently crosslinked in 35% humid air and b,d,f) swollen in deionized water.

the egg-box domains is stronger than a non-structured network. The larger the number of domains, the more difficult is to shear the network. When the fiber is immersed in water, water molecules are moving through the network, but the network is difficult to deform unless the domains break apart releasing calcium from the cage. Thus, the Ca^{2+} -crosslinked fiber is less water absorptive because the deformations are hindered by the rigid domains. In the covalently crosslinked fiber, calcium counter-ions are extracted from the material and exchanged with protons (or monovalent ions in saline solutions), resulting in the delamination of carboxylic groups. The ionic crosslinks in the amorphous and rigid domains are replaced by flexible acetal interchain crosslinks. When the fiber is exposed to water at pH above pK_a of alginate, the carboxylic groups dissociate and cause an additional expansion of the polymer network due to osmotic pressure of counter-ions entrapped in the fibers.^[17]

2.3. pH-Responsive Electric Conductivity

As mentioned, swelling of the alginate fibers is pH dependent. The swelling–shrinking transition is observed at pH 3.5 (Figure 4b,5) in accord with the pK_a values for the monomeric acids (3.38 and 3.65 for mannuronic and guluronic acid, respectively).^[11] Thus, the fibers are in the shrunken state below the pK_a , where the carboxylic groups are largely protonated and the polymer network is uncharged. In the swollen state above the pK_a , the same groups dissociate and produce an additional electrostatic contribution to osmotic pressure, causing the fibers to expand. Both the SWCNT-free and loaded fibers undergo the swelling–shrinking transition in the same pH range (Figure 5). Thus, the nanotubes do not affect the pH-transition range. However, the volumetric swelling ratio introduced as the

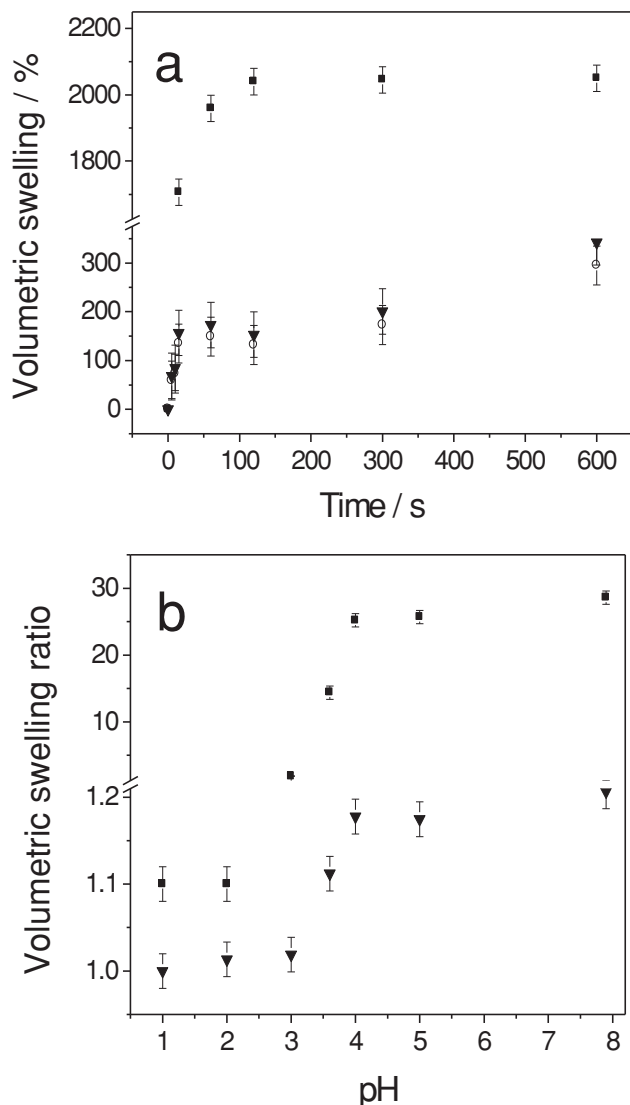


Figure 4. Swelling and pH responsive properties of alginate fibers: a) swelling dynamics in deionized water and b) volumetric swelling ratio vs the solution pH. Symbols: Ca²⁺-crosslinked, open circles; covalently crosslinked, solid squares; SWCNT-loaded and covalently crosslinked, solid triangles.

volume of a swollen fiber to the volume of a dry fiber does drastically change. For the SWCNT-free fibers the swelling ratio is about 20-fold greater than that of the SWCNT-loaded ones (Figure 4b). This behavior follows the Eshelby theory,^[18] suggesting that the SWCNT-reinforced fiber is expected to have a far greater shear modulus that restricts its swelling.

The SWCNT-loaded fibers are electroconductive.^[6c] We found that the fiber conductivity depends on the material swelling: the greater the swelling, the smaller is the conductivity. This behavior can be explained by the loss of contacts between the nanotubes when the matrix expands. There is an intriguing phenomenon observed with the covalently crosslinked fibers: the fibers reversibly deform during a swelling/shrinking cycle returning to the same level of conductivity after shrinking. This property of the SWCNT-alginate fibers is unique, and it does

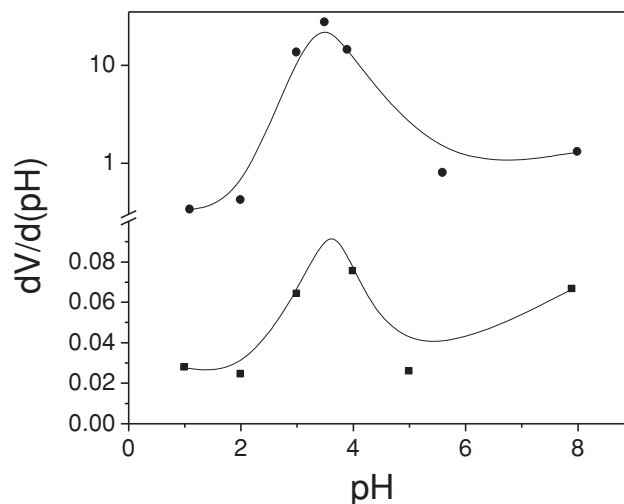


Figure 5. Differential plot for the pH-induced swelling transition of covalently crosslinked alginate fibers: SWCNT-free (solid circles) and SWCNT-filled (solid squares).

not have an analog among composite fibers; only a few ordered elastomers demonstrate this deformational reversibility,^[19] but we are not aware of any system that would reconstruct a network of carbon nanotubes after swelling. This unique reversible change of electroconductivity of the SWCNT-alginate fibers can be explained by a combination of two mechanisms: 1) water absorbing behavior of covalently crosslinked alginate network with deliberated carboxyl functional groups (note that ion-crosslinked composite fibers exhibit no sizable swelling) and 2) elastic deformation of the alginate network in the area of electrical contacts between SWCNT bundles arrested in the alginate matrix.

The swelling degree of covalently crosslinked alginate fibers depends on the pH and ionic strength of an aqueous solution via protonation-deprotonation equilibrium of carboxylic functional groups and screening of electrostatic interactions. Such a strong dependence of the swelling degree of covalently crosslinked fibers on the solution pH and ionic strength can be used to monitor these characteristics of solutions. In the experiments, a fiber fragment was bridged between two electrodes (forming electrical contacts with electrodes) and immersed in solutions of electrolytes at different pH values and ionic strengths. The 0.5 V potential versus a reference Ag/AgCl electrode was applied to the fiber. The electrical current in the SWCNT-filled fibers was found to be two orders of magnitude higher than the ionic current (Figure 6).

The pH and ionic strength dependent currents in the composite alginate fibers are shown in Figure 7. A reduction of the electrical current correlates with the volumetric swelling of the composite fibers: the greater the swelling degree, the smaller is the current. The ≈ 1.2 -fold pH-induced volumetric swelling results in a reversible disconnection between some SWCNT bundles in the composite, leading to about two-fold reduction of the fiber conductivity (Figure 8). Remarkably, the changes in the current were observed not only around the transition point (pH 3.5), but they were recorded in a broad range of pH values (from pH 1 to pH 11).

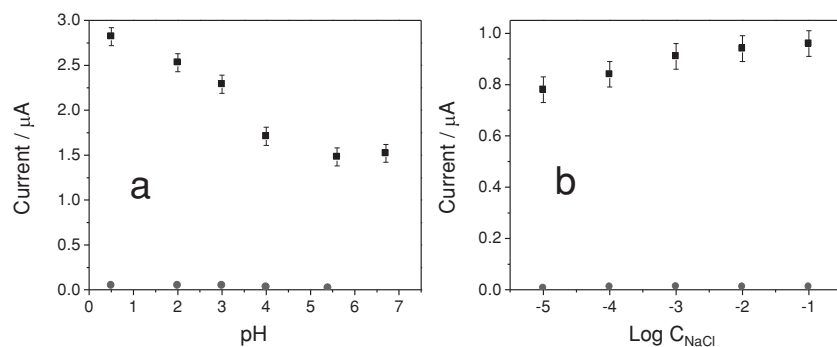


Figure 6. Electrical current in fiber samples immersed in aqueous solutions at different a) pH values (HCl) and b) NaCl concentrations for SWCNT-filled (solid squares) and SWCNT-free (solid circles) covalently crosslinked alginate fibers.

An increase in the ionic strength leads to electrostatic screening and shrinkage of the fibers. This, in turn, leads to recovery of electrical contacts between SWCNT bundles and to improved electrical conductivity (Figure 7b).

2.4. Humidity-Responsive Electric Conductivity

The alginate fibers (thoroughly washed in deionized water and dried) readily respond to humidity changes by altering their swelling degree (Figure 9). The humidity response of the alginate fibers is rapid, within fractions of a minute.

A covalently crosslinked fiber demonstrates a significantly higher sensitivity to changes in the relative humidity than the ionically crosslinked one. Hence, a unique combination of the covalently crosslinked alginate matrix and the SWCNT network aids to create a highly sensitive sensor platform enabling reliable detection of a 2% change in the air humidity. The resistance–humidity relationship is reproducible during many cycles of change of the relative humidity (Figure 10b).

2.5. Examples of Applications for Monitoring Aqueous Solutions and Humidity

Reciprocal reversible dependence between fiber swelling and electrical conductivity can be used for the development of

robust, inexpensive, disposable, and miniaturized sensors to monitor gases and liquids. Specifically, the composite fibers can be used to monitor physiological solutions and quality of water and air. The composite fibers are harmless for biological environment due to biocompatibility of the alginate matrix. The wet-spinning method is capable of producing continuous fibers that can be used to prepare textiles and non-woven mats or can be cut into pieces to fit various dimensions and design of sensor devices.

Here, we show some examples of the SWCNT-alginate fibers applications for monitoring physiological solutions and air. The monitoring of pH changes at the physiological

ionic strength (0.15 M) in sodium chloride solutions and monitoring changes of salt concentration at the physiological pH (pH 7.4) are demonstrated in Figures 11,7b, respectively. In both cases, the electrical current response was measured in a small section of the composite fiber. The sensor demonstrated a high sensitivity, $0.07 \mu\text{A pH-unit}^{-1}$ and $10^5 \mu\text{A M}^{-1}$ in ranges of pH 2 to pH 5 and salt concentrations from 10^{-5} to 10^{-1} M, which correspond to the important intervals of pH (e.g., inflamed and cancerous tissues) and salt concentrations (e.g., sodium in urine) found in different biological and biotechnological fluids, as well as variations of these parameters relevant to analysis of quality of water.

Another example demonstrates the application of the composite fibers for monitoring air humidity in a range from 5 to 95% (Figure 10) with the sensitivity of about $2.8 \mu\text{A \% RH}^{-1}$.

There are many different sensors proposed to monitor the pH, salt concentration, and humidity; however, the major advantage of the proposed sensor is in a combination of flexibility, ease manufacturing and calibration, biocompatibility, and disposability.

3. Conclusions

The SWCNT-loaded covalently crosslinked alginate fibers were prepared using wet-spinning of the SWCNT dispersions with alginate into the Ca^{2+} -enriched coagulation bath. The ionic crosslinking was then replaced by covalent crosslinking with

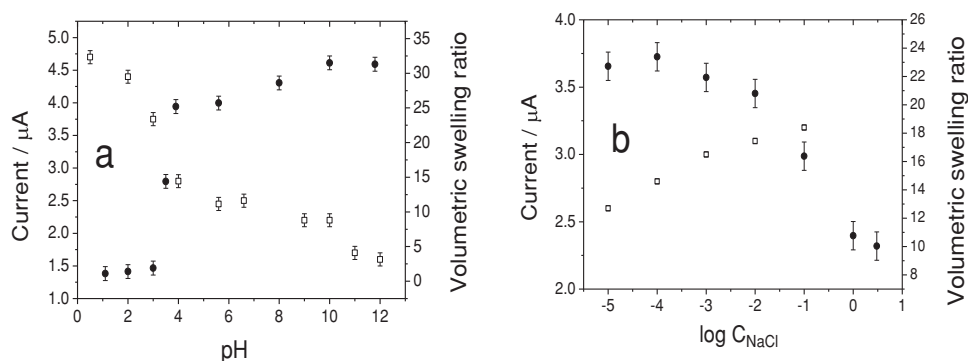


Figure 7. Electrical current (open squares) in SWCNT-loaded covalently crosslinked alginate fibers and their volumetric swelling (solid circles) in aqueous solutions at a) different pH and b) NaCl concentrations (in mole L^{-1}).

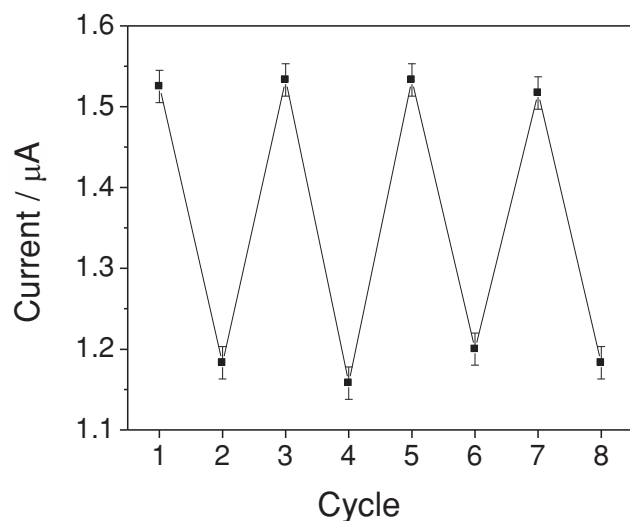


Figure 8. Electric conductivity of SWCNT-filled covalently-crosslinked alginate fibers upon cycling between pH 2 and pH 4.

glutaraldehyde. The fabricated fibers are electroconductive and responsive to humidity, pH, and ionic strength. Electrical conductivity of the fibers decreases as they imbibe water and swell. The reversible changes in the electrical conductivity are used

to monitor the relative humidity of the air environment from 5 to 95%, the pH in a range from pH 2 to pH 11, and the salt concentration in a range from 10^{-5} to 0.1 M.

The responsive properties of the fibers are due to a combination of the SWCNT network and stimuli-sensitive swelling properties of the covalently crosslinked alginate matrix. This mechanism provides a simple platform for conversion of the hydrogel responses into an electrical signal. The covalently crosslinked hydrogel preserves reversibility of the transition.

The fabricated SWCNT-alginate fibers can be incorporated into sensors of various architectures, textiles, wound healing materials, synthetic and biological implants, and can be used in aqueous, including physiological, environments. This versatility promises a number of intriguing applications of the developed stimuli-responsive material.

4. Experimental Section

An aqueous dispersion of 0.6% SWCNT (Nanoledge S. A., France) stabilized with sodium dodecyl sulfate (1.7%) and homogenized for 25 min using a horn sonicator was mixed with a 1.5% aqueous solution of sodium alginate (from brown algae, Sigma and MP Biomedicals USA) and stirred for 24 h. The prepared dispersion was wet-spun in a 15 wt% aqueous CaCl_2 solution at ambient conditions using an apparatus that consisted of a syringe pump set in the vertical syringe position and a CaCl_2 coagulation bath placed on an orbital shaker (Model DS-500, VWR).

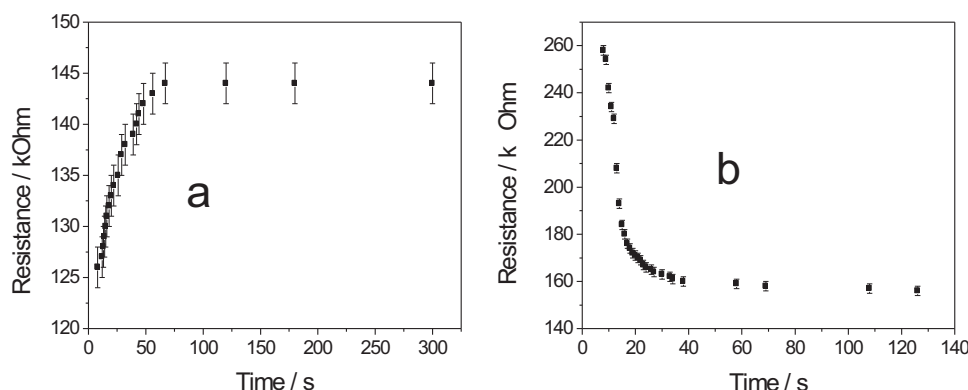


Figure 9. Humidity response of SWCNT-filled alginate fibers: time-dependent changes of resistance in response to changes in the relative humidity a) from 10% to 32% and b) from 85% to 32%.

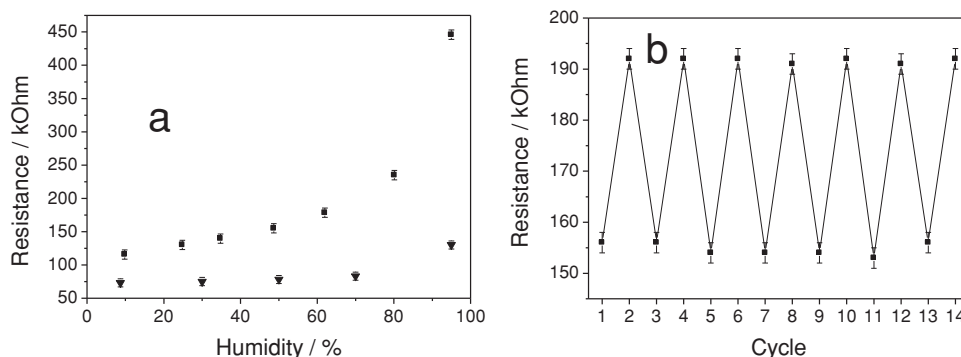


Figure 10. Electrical resistance of the SWCNT-loaded alginate fibers, ionic crosslinked with Ca^{2+} ions (solid triangles) and covalently crosslinked (solid squares): a) as a function of the relative humidity and b) upon cycling the relative humidity between 50% and 70%.

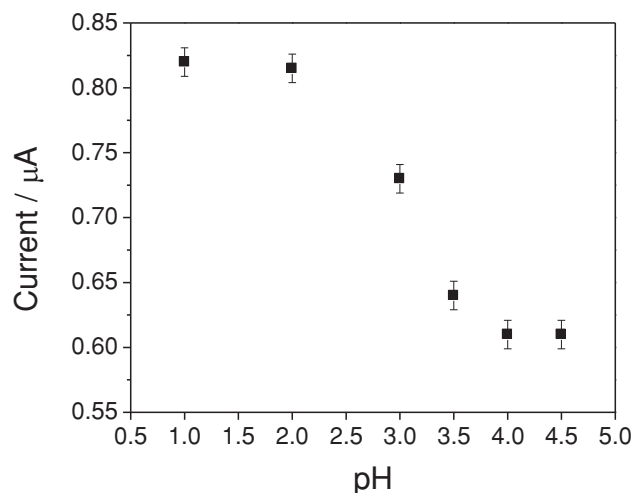


Figure 11. Electrical current in a SWCNT-filled alginate fiber sample immersed in aqueous 0.9% (0.15 M) NaCl solutions at different pH values (HCl).

Calcium ions caused immediate gelation of alginate which formed a continuous fiber coming out at the needle tip. The as-prepared fibers were incubated in 15% CaCl_2 for 30 min and then transferred to a 3% CaCl_2 solution for overnight treatment. Afterward the ionically crosslinked fibers were rinsed in water and dried in air.

In order to crosslink the fibers covalently, the composite alginate-SWCNT fibers were immersed in a water-acetone mixture (1:7.5 v/v) with 0.36 M glutaraldehyde and 50 mM HCl catalyst for 48 h at 40 °C. The fibers were washed in 0.1 M NaCl.

Electrical conductivity of the fibers was studied using 1–5 cm sections of a dry fiber that was glued by its tips to a glass slide using a conductive silver paint. The 0.5 V applied potential was applied to the fiber through the silver paint electrodes. In all experiments in solutions, all the conductive surfaces (except the fiber) were insulated with epoxy resin. Measurements of the resistance–humidity relationship were conducted in an environmental chamber with controlled relative humidity and temperature. Measurements of conductivity versus pH and concentration of NaCl were performed with a potentiostat in an electrochemical cell and an Ag/AgCl/Sat. KCl reference electrode.

For tensile test of the fiber, the ASTM D3822 Single fiber break method was performed using an Instron Tensile Testing Instrument. The gauge length was 1 cm and the testing speed was 10 mm min^{−1}. From the experimental data, the Young's modulus of the Ca^{2+} -crosslinked alginate fiber was found to be 1.55 GPa, whereas for the Ca^{2+} -crosslinked alginate fiber with 12 wt% carbon nanotubes it was 1.45 GPa. After covalent crosslinking, the tensile modulus of the fibers without nanotubes was found to be 2.04 GPa, and for the fibers with 12 wt% nanotubes it was 2.2 GPa.

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