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A One-Step Method of Hydrogel Modification by Single-Walled Carbon Nanotubes for Highly Stretchable and Transparent Electronics

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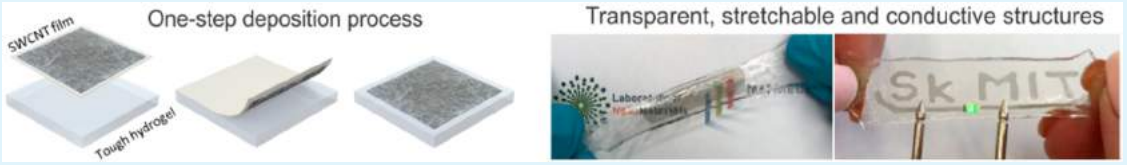
Supporting Information



ABSTRACT: Electrically conductive hydrogels (ECHs) are attracting much interest in the field of biomaterials science because of their unique properties. However, effective incorporation and dispersion of conductive materials in the matrices of polymeric hydrogels for improved conductivity remains a great challenge. Here, we demonstrate highly transparent, electrically conductive, stretchable tough hydrogels modified by single-walled carbon nanotubes (SWCNTs). Two different approaches for the fabrication of SWCNT/hydrogel structures are examined: a simple SWCNT film transfer onto the as-prepared hydrogel and the film deposition onto the pre-stretched hydrogel. Functionality of our method is confirmed by scanning electron microscopy along with optical and electrical measurements of our structures while subjecting them to different strains. Since the hydrogel-based structures are intrinsically soft, stretchable, wet, and sticky, they conform well to a human skin. We demonstrate applications of our material as skin-like passive electrodes and active finger-mounted joint motion sensors. Our technique shows promise to accelerate the development of biointegrated wearable electronics.

KEYWORDS: *single-walled carbon nanotubes, tough hydrogels, stretchable electronics, electrically conductive hydrogel, dry transfer*

INTRODUCTION

Hydrogels are novel soft materials that have enabled diverse modern technologies, including tissue engineering,[1−3] drug delivery,[4] biomedical devices,[5] microfluidics,[6,7] stretchable and biointegrated electronics,[8] and soft robotics.[9,10] Remarkable progress has been made by researchers in the synthesis and fabrication of hydrogels across a range of various applications. As a result of the high stretchability and fracture toughness of hydrogels,[6] intensive efforts have been devoted to developing various biomimetic structures and devices based on them.[6,8,11−13] Furthermore, hydrogels with similar physiological and mechanical properties to a human skin represent an ideal material for electronics and devices to achieve long-term effective biointegrations.[14,15]

Electrically conductive hydrogels (ECHs)[16−18] are usually produced in the form of layered structures consisting of hydrogels and conductive fillers such as silver nanowires,[19] PEDOT:PSS,[20] graphene,[21] etc. However, such materials do not possess desired mechanical robustness, which limits the stretchability of ECHs. Single-walled carbon nanotubes (SWCNTs) are a unique family of materials exhibiting exceptional thermal, electronic and mechanical properties.[22] In addition, as a result of a regular pore structure, excellent electrochemical stability, well-defined one-dimensional structure, low mass density, high mechanical strength, and high specific area, SWCNTs have been utilized as nanofillers of nanocomposite hydrogels.[23−26] However, an effective incorporation and dispersion of SWCNTs in the matrices of polymeric hydrogels remain a great challenge due to their agglomeration and the presence of surfactants.

Here, we demonstrate a one-step technique of hydrogel surface modification with conductive SWCNT films. This technique allows us to utilize high water content and transparency with good electrical and mechanical properties without loses in both SWCNTs and hydrogel functionalities. Using this approach, we realize mechanically robust, highly

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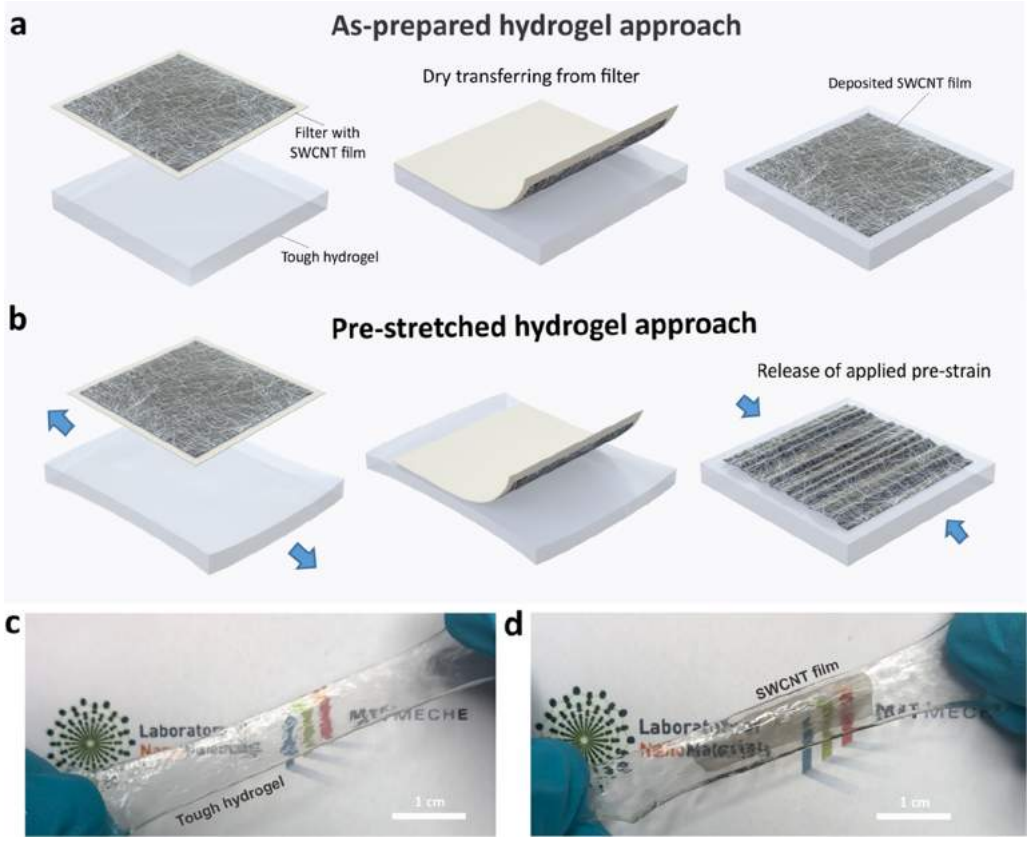

Figure 1. Generic illustration of the SWCNT film deposition process realized by two dry transfer approaches: (a) on the as-prepared tough hydrogel surface; (b) on the pre-stretched surface. SWCNT/hydrogel structure functional properties: photographs of (c) tough hydrogel and (d) SWCNT/hydrogel structure at the stretched state demonstrating its high transparency.

stretchable, biocompatible,[5] conductive, and transparent SWCNT/hydrogel structures and demonstrate their applications as finger-mounted joint motion sensors and electrocardiographic electrodes. The advantages of the proposed structures in terms of conductivity, stretchability, transparency, and applicability for electronic circuit creation are highlighted in Table S1.

RESULTS AND DISCUSSION

SWCNTs are synthesized by the aerosol (floating catalyst) CVD method described elsewhere.[27] SEM and TEM images of the obtained SWCNT films are presented in Figure S1. SWCNT films used in this study have a thickness of approximately 40 nm (with an optical transmittance of 80% at 550 nm). After the SWCNT film on a nitrocellulose filter is cut in a desired shape, it is simply pressed against the tough hydrogel. As SWCNTs have low adhesion to a nitrocellulose filter, the filter is easily peeled off, leaving the SWCNT film on the surface of the hydrogel. A step by step process of the SWCNT deposition is illustrated in Figure S2.

Figure 1a,b shows the SWCNT film deposition process on a hydrogel surface, which can be implemented in two ways. The first approach is based on a simple transfer of the SWCNTs from a filter onto the as-prepared hydrogel surface (Figure 1a), while the second one is based on pre-stretching of the hydrogel before the SWCNT film deposition (Figure 1b). The photographs of the stretched tough hydrogel and obtained SWCNT/hydrogel structure are presented in Figure 1c. This demonstrates the high transparency of the SWCNT/hydrogel structures, which is retained even in the stretched state (Figure 1d).

Electrical, optical, and morphological properties of the SWCNT/hydrogel structures, fabricated by both approaches, are further investigated. After the SWCNT film deposition by the first approach, our structure was ready to be further examined in a special stretching device. For two-point resistance measurements, 2 × 0.5 cm^2 hydrogel samples and SWCNT films of the same size are used. Figure 2a demonstrates the electrical properties of the SWCNT films under stretching/releasing cycles with 15, 30, 50, and 100% strains applied. Relative change in the resistance of the SWCNT films between stretched and released states are about 40, 80, and 300% for strains ε = 15, 30, and 50%, respectively. When the highest value of strain (ε = 100%) is applied, the resistance reaches 28 kΩ (compared to the initial one of 200 Ω), which can be explained by the appearance of microcracks, visualized by an optical microscope (Figure 2d). The sheet resistance of the SWCNT/hydrogel structures and SWCNTs on glass, PET, and PDMS substrates measured by a four-probe method is almost the same in the relaxed state (around 100 Ω/□). In the stretched state (at 50% strain applied before crack formation), sheet resistance of the SWCNT/hydrogel structure is comparable to the values obtained for the SWCNTs deposited onto the PDMS substrate (around 350 Ω/□). After the cracks appear in the SWCNT film, the resistance remains in the range of 16−18 kΩ. However, we demonstrate stable behavior of fabricated SWCNT/hydrogel structures, which is observed during 5000 stretching/releasing cycles, while 30% strain is applied. On the basis of the performed character-

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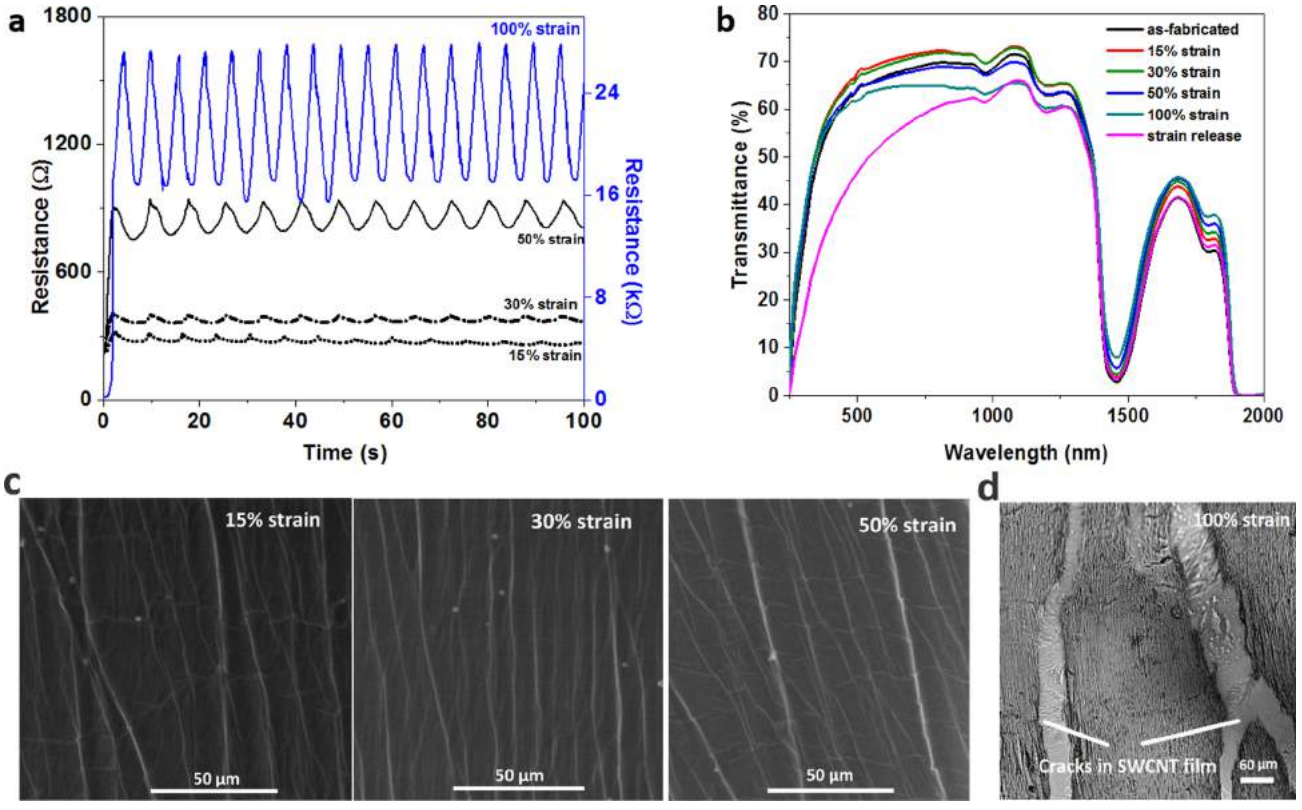

Figure 2. Characterization of SWCNT/hydrogel structures prepared by deposition onto the as-prepared hydrogel: (a) resistance change during several stretching/releasing cycles up to 15, 30, 50, and 100% strains applied, (b) transmittance spectra at different strains, (c) SEM images after 15, 30, and 50% strains applied, and (d) optical microscopy image of SWCNT film after the 100% strain applied.

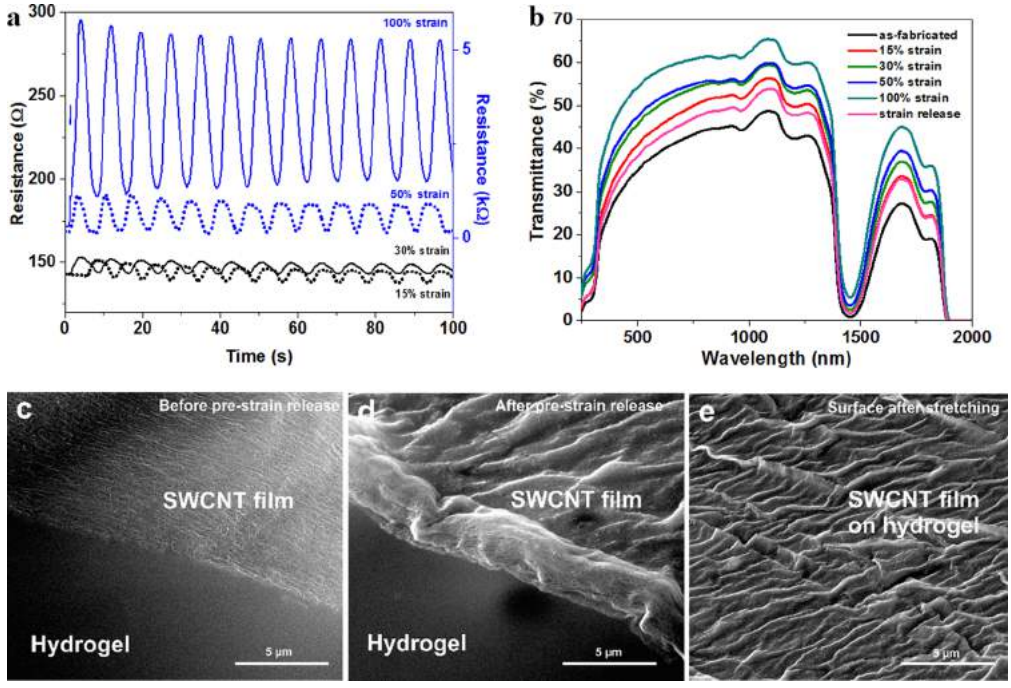

Figure 3. Characterization of SWCNT/hydrogel structures prepared by deposition onto the pre-stretched hydrogel (the pre-strain value is 30%): (a) resistance change while 15, 30, 50, and 100% strains are applied, (b) transmittance spectra at different strains. SEM images of SWCNT/hydrogel structure morphology: (c) before release of the hydrogel pre-strain after SWCNT film deposition, (d) after release of the hydrogel prestrain, (e) after 15 cycles of stretching to 30% strain.

ization, it may be proposed that such SWCNT/hydrogel structures can be used for strain-sensitive applications.[24]

Transmittance spectra of the SWCNT/hydrogel structures are presented in Figure 2b. The transmittance value at the

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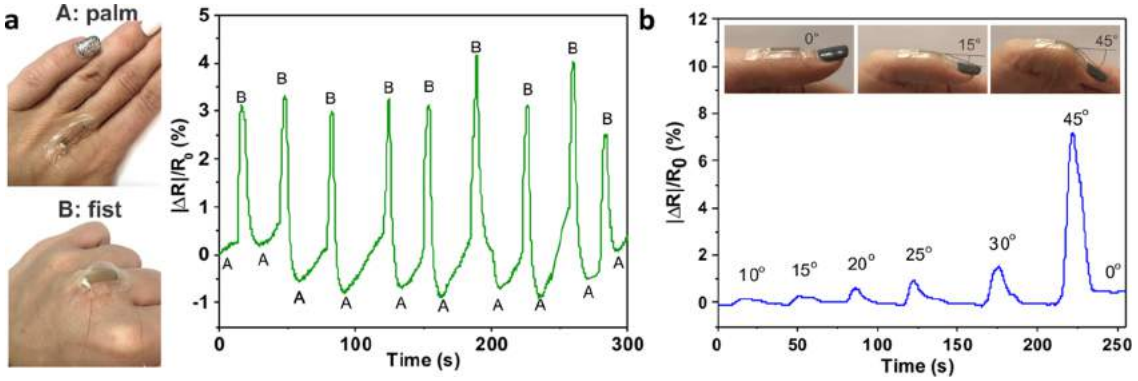

Figure 4. Application of SWCNT/hydrogel structures as active components: (a) biocompatible strain sensors for human motion detection: resistance change of the SWCNT/hydrogel structure attached to a human arm under repeatable bending cycles, (b) resistance change of a SWCNT/hydrogel electrode attached to a human finger depending on the bending angle.

wavelength of 550 nm decreases with the increase of the applied strain (Figure S4a). This can be explained by the increase of the scattering in the hydrogel structure while stretching (Figure S5). The scanning electron microscopy (SEM) images of the SWCNT networks after 15, 30, and 50% strains applied are shown in Figure 2c. SEM studies of the SWCNT/hydrogel structures confirm a slightly changed morphology of SWCNTs after application of these strain values.

The same characterization is conducted for the second approach with the SWCNT/hydrogel structures on hydrogel pre-stretched to ε = 30%. It is confirmed that the procedure of the hydrogel substrate pre-stretching before the SWCNT film deposition allows us to exploit formed wrinkles for stable and highly stretchable electronic components. A relative change in the resistance of the SWCNT film between stretched and released states is about 7% for 15 and 30% strains applied (Figure 3a). When the strain is higher than the pre-stretching strain value, we observe a significant increase of the resistance of about 10 times at ε = 50% and 60 times at ε = 100% applied. However, the resistance value at the 100% strain is still lower for the pre-stretching approach (R = 6 kΩ) than that for the as-prepared hydrogel approach (R = 30 kΩ). The transmittance spectra of the SWCNT/hydrogel structures (Figure 3b) demonstrate an increase in the transparency with the applied strain. This can be explained by the process of wrinkle removal leading to the improvement of the overall transmittance (from the initial value of 37 to 57% while stretched to ε = 100%). Thus, the pre-stretching approach allows us to improve the transmittance of the whole structure at the stretched state. Moreover, after the strain release, the transmittance returns back to the value of 40%, which is close to the initial one (Figure S4b). Thus, the pre-stretching of the hydrogel before SWCNT deposition makes it possible to overcome the low conductivity at high strains and ensure high transparency. SEM images of the SWCNT/hydrogel structures before pre-stretching and after the strain release are shown in Figure 3c–e. From these images, we can observe an excellent adhesion of the SWCNT films to the hydrogel surface before stretching and after the strain release. It is worth noting that the demonstrated approach of the SWCNT/hydrogel structures fabrication can be utilized for applications, where stable performance of the electrodes during stretching is needed without the alteration of the electrical properties.

The resistance (R_l) of the SWCNT/hydrogel structures during stretching is estimated by the eq 1[28]

$$R_l = \frac{l}{\sigma_l t_l w_l} \tag{1}$$

where σ_l is the electrical conductivity of the SWCNT/hydrogel structures at a certain strain; l, w_l, and t_l are length, width, and thickness of the sample, respectively, at a certain strain.

Here we use two assumptions: (i) electrical resistivity of the structure is constant while stretching; (ii) relative change in the SWCNTs and hydrogel dimensions, such as width and thickness, are the same and can be found as[29]

$$l = l_0(1+\varepsilon); \quad w_l = w_0(1+\varepsilon)^{-\nu}; \quad t_l = t_0(1+\varepsilon)^{-\nu} \tag{2}$$

where l_0, w_0, and t_0 are the length, width, and thickness of the structure before stretching; ε is applied strain value; ν is Poisson's ratio (ν = 0.4 for tough hydrogel).

Using eq 2 and two assumptions, we can express R_l in terms of the stretching

$$R_l = R_0(1+\varepsilon)^{1+2\nu} \tag{3}$$

where R_0 is the electrical resistance of the SWCNT/hydrogel structures before stretching.

We use eq 3 to compare the experimental results and theoretical prediction for the SWCNT/hydrogel resistance change during stretching. The results (Figure S3c) reveal a good agreement of the theory with the prestretched approach and thus stable adhesion of the SWCNTs to hydrogel, which can be explained by the appearance and removal of the SWCNT wrinkles confirmed by the SEM images. However, disagreement of the theory with the as-fabricated approach is demonstrated as a result of the structural changes and crack formation in the SWCNT film while stretching.

The fabricated transparent, stretchable, and electrically conductive SWCNT/hydrogel structures can find a variety of applications as active and passive components, where on one hand high sensitivity to the external force is desired, and on the other one, stable performance of the electrical circuit is needed. Such an effect can be achieved by using two different deposition techniques, whether SWCNT films are transferred onto the as-fabricated tough hydrogel surface or onto the pre-stretched one, respectively. Thus, both approaches are based on a simple and dry transfer technique, which allows utilization of the same material (SWCNT films) as a stable electrical

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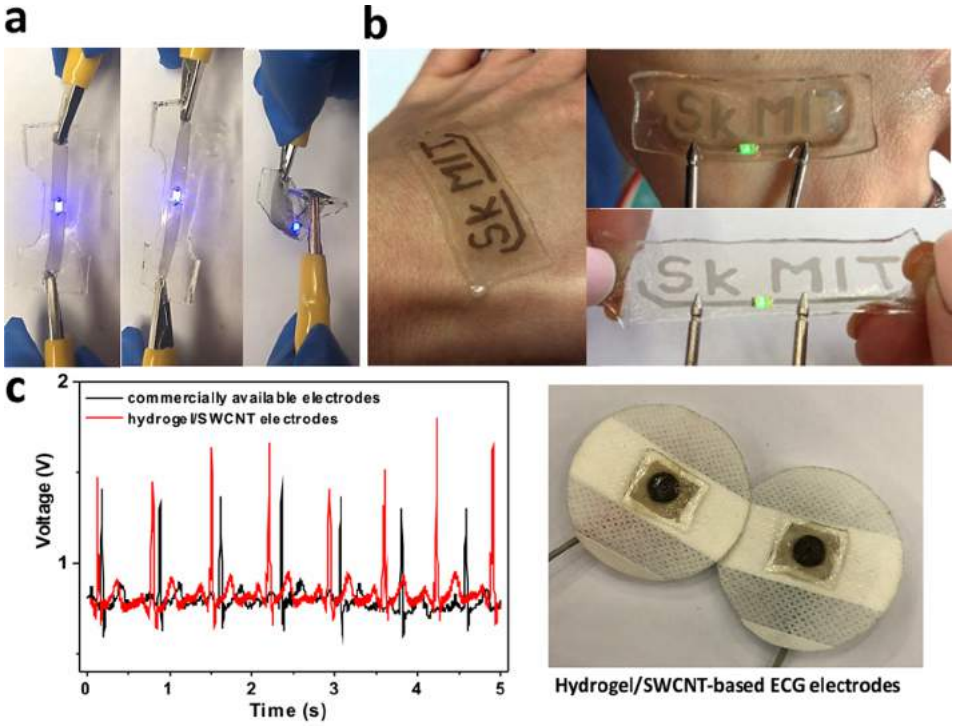

Figure 5. Application of SWCNT/hydrogel structures as passive electrodes: (a) stretchable LED-based circuit with conductive SWCNT contacts at different stretched and twisted states, (b) SWCNT/hydrogel-based patterned circuits at a relaxed state and stretched to 50%, (c) biocompatible electrodes for ECG signal measurements with photographs of SWCNT/hydrogel electrodes.

conductor and a sensitive detector. To demonstrate potential applications of our novel material, we develop a stretchable human motion detector based on the SWCNT transfer onto the as-fabricated tough hydrogel and attach the SWCNT/hydrogel electrodes (by the hydrogel side) to an arm or to a finger (Figure 4a,b). To avoid mechanical failure at the junction between the stretchable SWCNT/hydrogel structures and rigid wires for signal processing, we use an adhesive medical patch so that the hydrogel directly adhere to the skin. After the fabrication, sensors are attached onto the target places (knuckles and finger flexor). As a result, the skin and SWCNT/hydrogel sensor behave as a single cohesive stretchable object, and deformation of the skin can be directly monitored. To detect the relative resistance change from a palm to a fist (relaxed state of the arm (A) and clenched into a fist (B)), we fabricate a SWCNT/hydrogel strain sensor with a 30×5 mm^2 sensing area (Figure 4a). In order to control small motions, such as particular finger flexing, we fabricate a SWCNT/hydrogel strain sensor with a 10×5 mm^2 sensing area (Figure 4b). Thus, various types of skin strains can be monitored by the upward and downward trends of the relative resistance data plots. One of the most promising advantages of such devices is the option for repeatable and constant use of the sensor, which does not restrict motions. Proposed SWCNT/hydrogel structures could be used for implantable electrodes by simple encapsulation with the top layer of hydrogel, as they are kept hydrated during the implantation because of their water content.

On the basis of the second pre-stretching approach, we fabricated SWCNT/hydrogel based passive electrodes. Figure 5a illustrates a rigid LED-based electronic circuit, which can be mechanically deformed. Previously it has been achieved by a wire connection of LED arrays,[5,8,30] which is rigid and has complicated technology to allow the stretchabilty. Our approach is a novel method of electrical circuit creation, which allows fabrication of biocompatible, transparent, and robust electrodes, stable under large deformations and applicable for different wearable electronic devices. Validation of the performance of the SWCNT/hydrogel structures in an electrical circuit is confirmed by a constant intensity of an LED light under the applied strain. Practically, SWCNT film patterns of any size and shape can be used for different wearable and skin-like devices (Figure 5b). As one more example, we fabricated a stable electrode for continuous monitoring of electrocardiography (ECG) signals and its long-term variability, which has improved signal-to-noise ratio (35 dB) compared to commonly used ECG electrodes (30 dB) (Figure 5c). The fact that hydrogels are intrinsically wet will allow them to remain breathable and allow for robust skin contact, revealing its safety for biomedical applications. While hydrogels consist of an ionic cross-linker, such material can been used as transparent ionic conductor, connected to the skin.

CONCLUSION

In summary, we report new transparent, stretchable, conductive, and biocompatible hydrogels modified by SWCNT films to create passive electrodes and active sensors for wearable and skin-like electronics. We introduce here a one-step, universal, and applicable method for SWCNT/hydrogel structure fabrication, withstanding intrinsic stretching up to 100% strain. Our method holds advantages, compared to those reported previously, as it is a direct transfer from the filter onto a hydrogel surface without the need for a sacrificial layer or any other intermediate steps. It is performed at ambient conditions onto an aqueous hydrogel surface. We applied our approach to the creation of a new set of soft and

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robust components, such as electrodes for ECG monitoring and active sensors for a human motion detection. Our method of the SWCNT films patterning allows the creation of large-area electronic circuits. Moreover, it has the potential to be used for various tissue engineering or sensing applications as well as for a variety of wearable devices, including electronic skins.

EXPERIMENTAL SECTION

We utilized SWCNT films produced by an aerosol (floating catalyst) CVD method.[27] Briefly, this method is based on ferrocene vapor thermal decomposition in the atmosphere of CO at the temperature of 880 °C. The as-synthesized SWCNTs were collected downstream of the reactor by passing the flow through microporous nitrocellulose filters.

Tough hydrogels utilized in this work were synthesized according to a previously reported protocol.[25,26] A precursor solution was prepared by mixing 4.1 mL of 4.8 wt % alginate (Sigma, A2033) and 5.5 mL of 18.7 wt % acrylamide (Sigma, A8887). We added 0.2 g of *N*,*N*-methylenebis(acrylamide) (Sigma, 146072) as the cross-linker for polyacrylamide and 102 μL of 0.2 M ammonium persulfate (Sigma, 248 614) as an initiator for polyacrylamide. After degassing the precursor solution in a vacuum chamber, we added 200 μL of 1 M calcium sulfate (Sigma, C3771) as the ionic cross-linker for alginate and 8.2 μL of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (Sigma, T7024−50M) as the cross-linking accelerator for acrylamide. Thereafter, the precursor solution was poured into an acrylic mold and was subjected to ultraviolet light for 60 min with 8 W power and 254 nm wavelength to cure the hydrogel.

After deposition, the SWCNT/hydrogel structures were simultaneously tested (homemade stretching device) with two-wire resistance measurements (Digital Multimeter Keysight 34410A). Both edges of the hydrogel substrate with the deposited SWCNT film (Figure S3a) were fixed under the clips of a stretching device (Figure S3b). The morphologies of the SWCNT/hydrogel structures were investigated using an FEI Versa Dual Beam scanning electron microscope (environmental mode) with a special tensile stage Gatan 200N for an in situ visualization of stretching/releasing processes. TEM images were obtained with a Tecnai G2 F20 transmission electron microscope with a point resolution of 0.24 nm at 80 kV. For the characterization of optical properties, transmittance of the samples was measured by Lambda 1050 UV−vis−NIR spectrophotometer at the 350−2000 nm wavelength range. The scattering spectra (diffusive part of full transmittance) of the hydrogel at different stretched states were measured using a spectral response measurement system, Bentham PVE300. The system is equipped with DTR6 integrating sphere (Ba_2SO_4-coated, 150 mm in a diameter) with an approximately 2.5×2.5 mm^2 monochromatic probe beam on the working plane of a sample.

In order to fabricate patterned SWCNT films on a hydrogel surface, demonstrated in Figure 4, we used the following technique. A template of the SWCNT film pattern was created by graphical software and processed by the CO_2 laser cutting machine (GCC LaserPro Spirit GLS) and computer printing tool. The SWCNT film was patterned according to the created image of the desired circuit by simple burning of the SWCNTs at undesired places. Further hydrogel substrate was pressed against the patterned SWCNT films, and after the deposition, a nitrocellulose filter was peeled off from the surface. A small amount of conductive silver paste was used in order to make contact between the SWCNT film and rigid case of LED.

For ECG signal measurements, the AD8232 integrated signal conditioning block was used. A three-electrode configuration was realized for signal processing, where first commercially available ECG electrodes were connected to the right and left hands and right foot. After that, SWCNT/hydrogel-based electrodes were attached to the same places.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b08409.

Comparison between different electrically conductive hydrogels, SEM and TEM images of SWCNTs, SWCNT film deposition process, theoretical prediction for the relative resistance change of the SWCNT/hydrogel structures, optical properties of hydrogels and SWCNT/hydrogel structures, stability test for the resistance of SWCNT/hydrogel structure (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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