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Highly Stretchable Multi-Walled Carbon Nanotube/Thermoplastic Polyurethane Composite Fibers for Ultrasensitive, Wearable Strain Sensors

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Contents

EXPERIMENTAL SECTION

Materials

Multi-walled carbon nanotubes (MWCNTs, TMC 220-10, Diameter: 8~15 nm, Length: 5~20 μm, purity: ~95% wt.%) were purchased from Nano Solution, Korea. Thermoplastic polyurethanes (TPU) (80A) was obtained from Bayer Company (Germany). Polyester-based TPU (code Elastollan 1185A) was provided by BASF Co. Ltd. N,N-Dimethylformamide(DMF, 99.8 %), dicyclohexyl carbodiimide (DCC, 99 %) and sodium dodecyl sulfate (SDS, 99%) were purchased from Sigma-Aldrich. Acetone (99.5%) was purchased from Samchun Pure Chemical Company.

Synthesis of Highly Stretchable CNTs reinforced TPU fibers

3 g MWCNTs were dispersed into 97 g DMF solution (contains of DCC and SDS) to form uniformly 3 wt % MWCNTs DMF suspension under sonication for 2 h. To obtain different MWCNT-to-TPU weight ratios, TPU particles with the desired weight were added into suspensions and DMF was added to keep TPU about 8 wt % in the solution. Then the solution was kept at 95 °C overnight, the MWCNT/TPU suspension could be used for the wet spinning process after cooling to room temperature. In this research, the MWCNT-to-TPU weight ratios of the prepared suspensions were 1:1, 1:3, 1:4, 1:5, 1:6, 1:8, 1:12 and 1:20, respectively. Such prepared suspension was extruded into an acetone based (5 vol % DMF in acetone) coagulation solution by a syringe through a spinneret with an inner diameter of 340 μm and the continuous fiber was collected on an aluminum foil drum (movie S1). The obtained fibers were immersed into water at 80 ^{o}C for about 2h to remove the residual solvents existing in the composite fibers. Finally, the fibers were collected on thread spools as shown in Figure 1a.

Characterization

Optical and SEM images were taken by the optical microscopy (Nikon Eclipse Lv150N), scanning electron microscope (SEM, SNE 4500M, SEC, Korea) and Field emission scanning electron microscopy (FESEM, JSM-6700F, JEOL, Japan), respectively. Stress-strain curves of the composite filament were obtained using a TA Instruments Q800 Dynamic Mechanical Analyzer (DMA). Detailed information can be found in our recent work.

Electromechanical Response Measurement of the Fiber

To test the strain-sensing characteristics, a single fiber was attached on the motorized moving stages (Ecopia, Step Motor Controller, FS100801A1P1) by copper scotch, and then uniform stretch/release cycles were applied to the samples while the electrical response of the sensor was recorded by a digital Source Meter (Keithley 2100) or a potentiostat (VSP-300 - Bio-Logic).

Weight-to-strain Sensors

A weight-to-strain cloth sensor was assembled by weaving the MWCNT/TPU fibers. A 11× 11 matrix was woven by MWCNT/TPU fibers with the distance of 5 mm to measure 2D resistances change in this experiment. When the objects are positioned on the cloth sensor, the strain change resulting from the weight could be monitored the object's shape by measuring the resistance change. Moreover, our weight-to-strain cloth sensor could detect the shape of the objects individually and precisely. The resistance changes of the fiber crosses were also recorded by a digital Source Meter.

3 Lines Wire-type Strain Sensors for Human Activities Monitor

The MWCNTs reinforced composite fiber was stitched on the elastic bandage with a cotton yarn using a sewing machine(**Fig. S10**). Specifically, the fibers were connected with conductive wires using silver paste and fixed by conductive tape and medical tape. For the monitoring of human activity, the resistance changes of wire-type strain sensor-based electronic skin were recorded by a digital Source Meter (Keithley 2100) every 100 ms.

Smart Glove

A smart glove was assembled with ten individual fiber-type strain sensors, with two sensors on each finger (I on Bouchard's nodes, II on Metacarpophalangeal joints), which could monitor real-time motions of fingers. The smart glove is integrated with a custom-made data acquisition system with wire communication modules. Moreover, our smart glove could detect the motion of each finger individually and precisely. The resistance-changed curve of our integrated smart glove device was recorded by a digital Source Meter (Keithley 2100) to detect gestures.

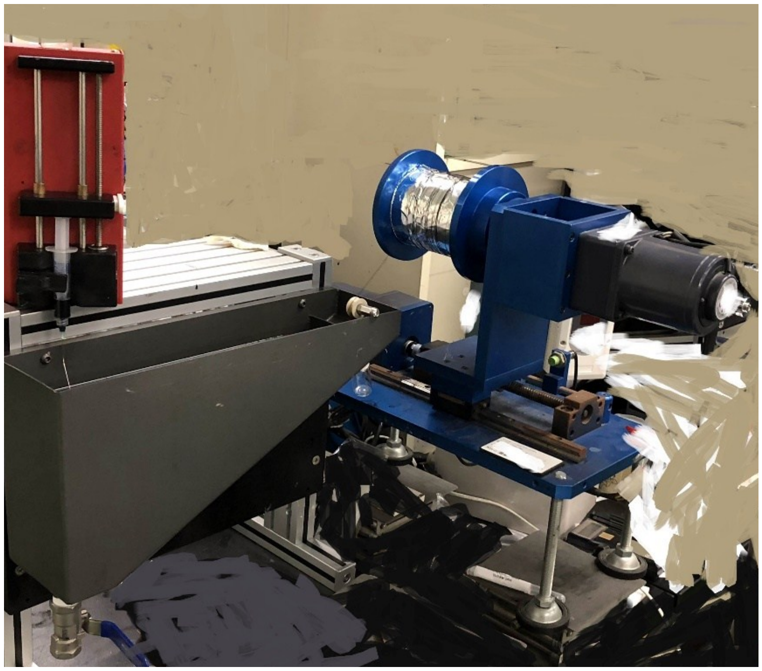

Figure S1 Photograph of the experimental setup for wet spinning.

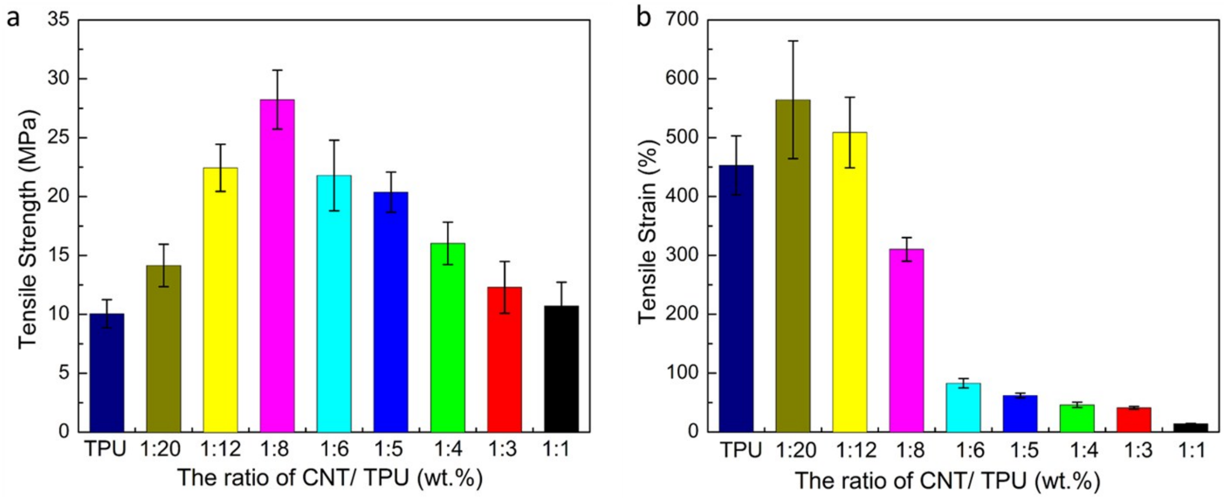

Figure S2 Tensile strength plots(a) and maximum failure strain plots(b) of the MWCNT/TPU fibers with different weight ratios of MWCNTs and TPU.

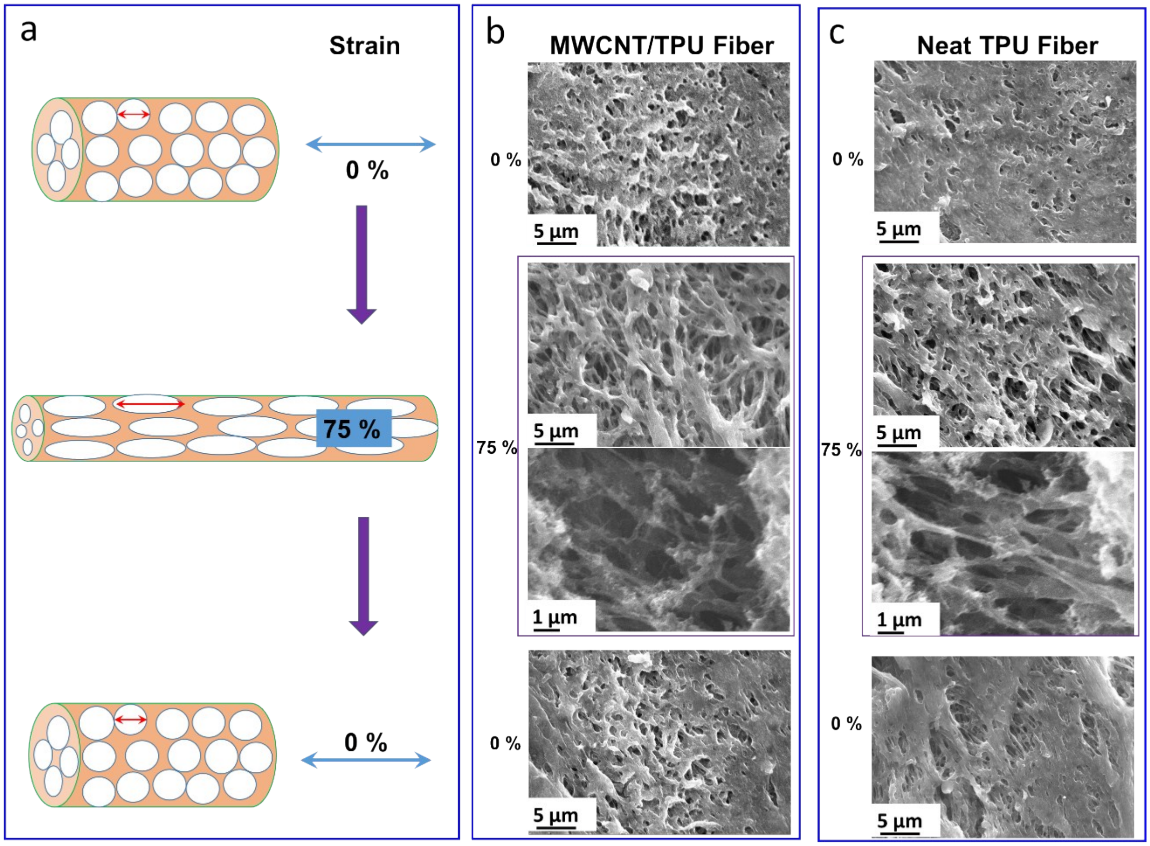

Figure S3 Structure changes in the porous composite fibers during a stretch/ release circle: a, schematic illustration of the porous structural changes; b-c, SEM images of structure changes in high magnification of MWCNT/TPU fiber and neat TPU fiber.

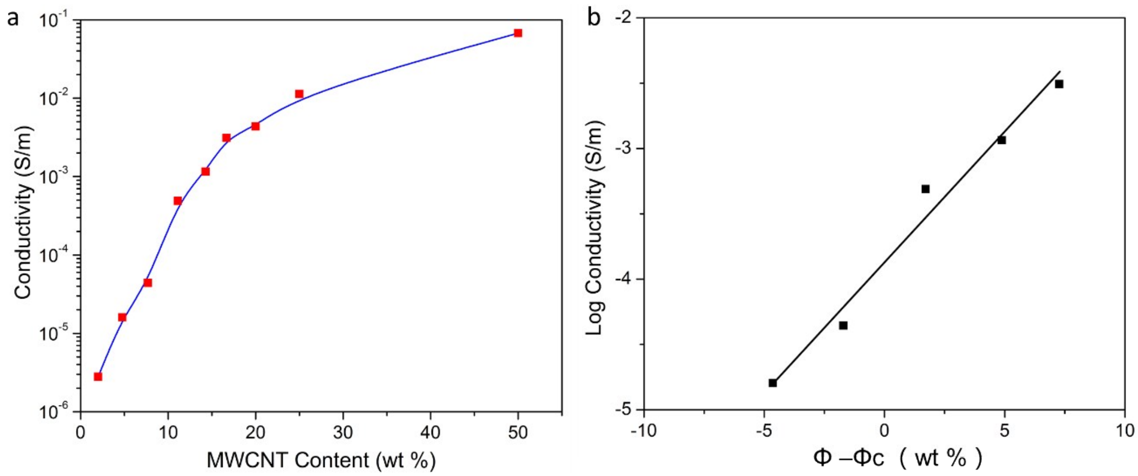

Figure S4 (a) Electrical conductivity of the MWCNT/TPU fibers versus filler concentration and (b) the fitting of experimental data using the classical percolation theory.

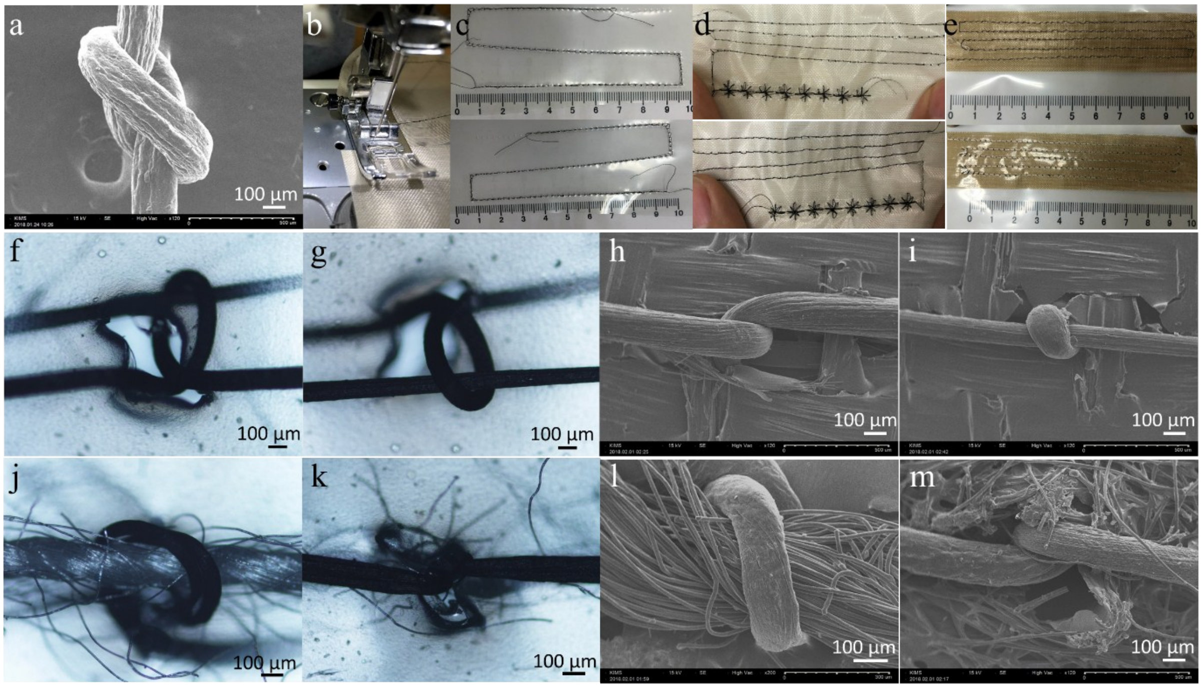

Figure S5 (a)The tightly knotted MWCNT/TPU fiber; (b-m) Sewing images of MWCNT/TPU Fibers with MWCNT-to-TPU weight ratio of 1:8.

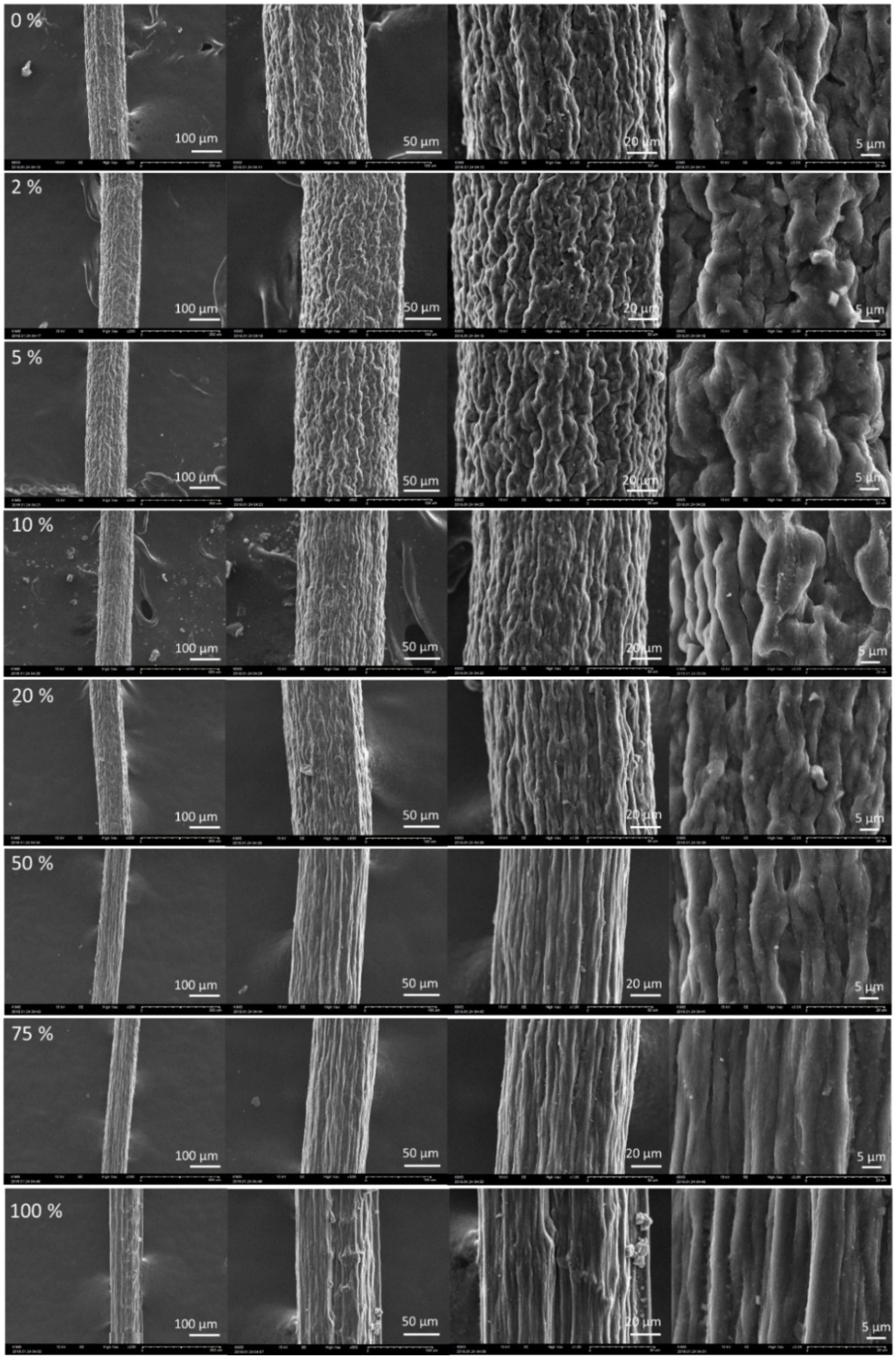

Figure S6 SEM images of MWCNT/TPU fibers with the weight ratio of 1:8 under different stretch ratios.

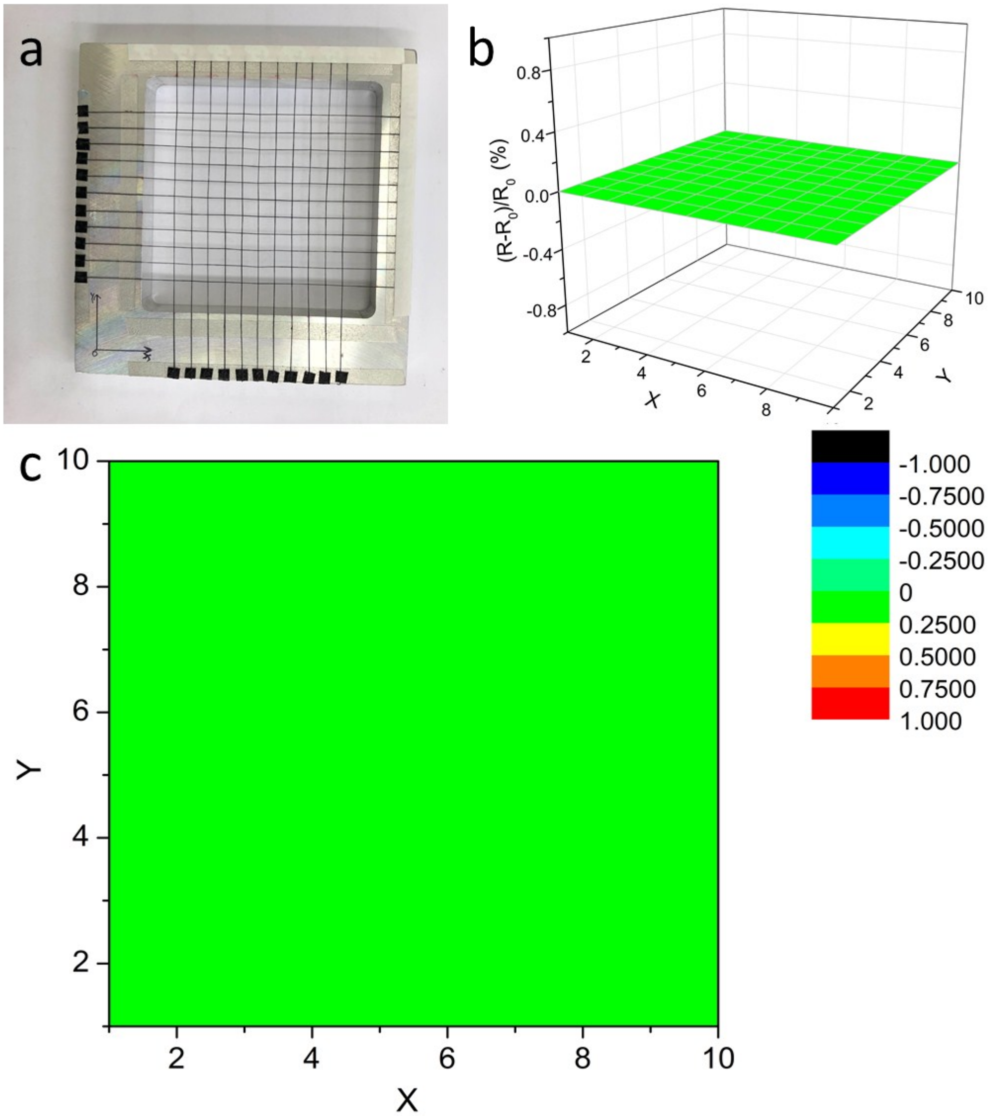

Figure S7 (a) Photograph of weight-to-strain sensor based on the cloth woven by MWCNT/TPU fibers, (b-c) the resistance responses of the sensor without anything on the cloth.

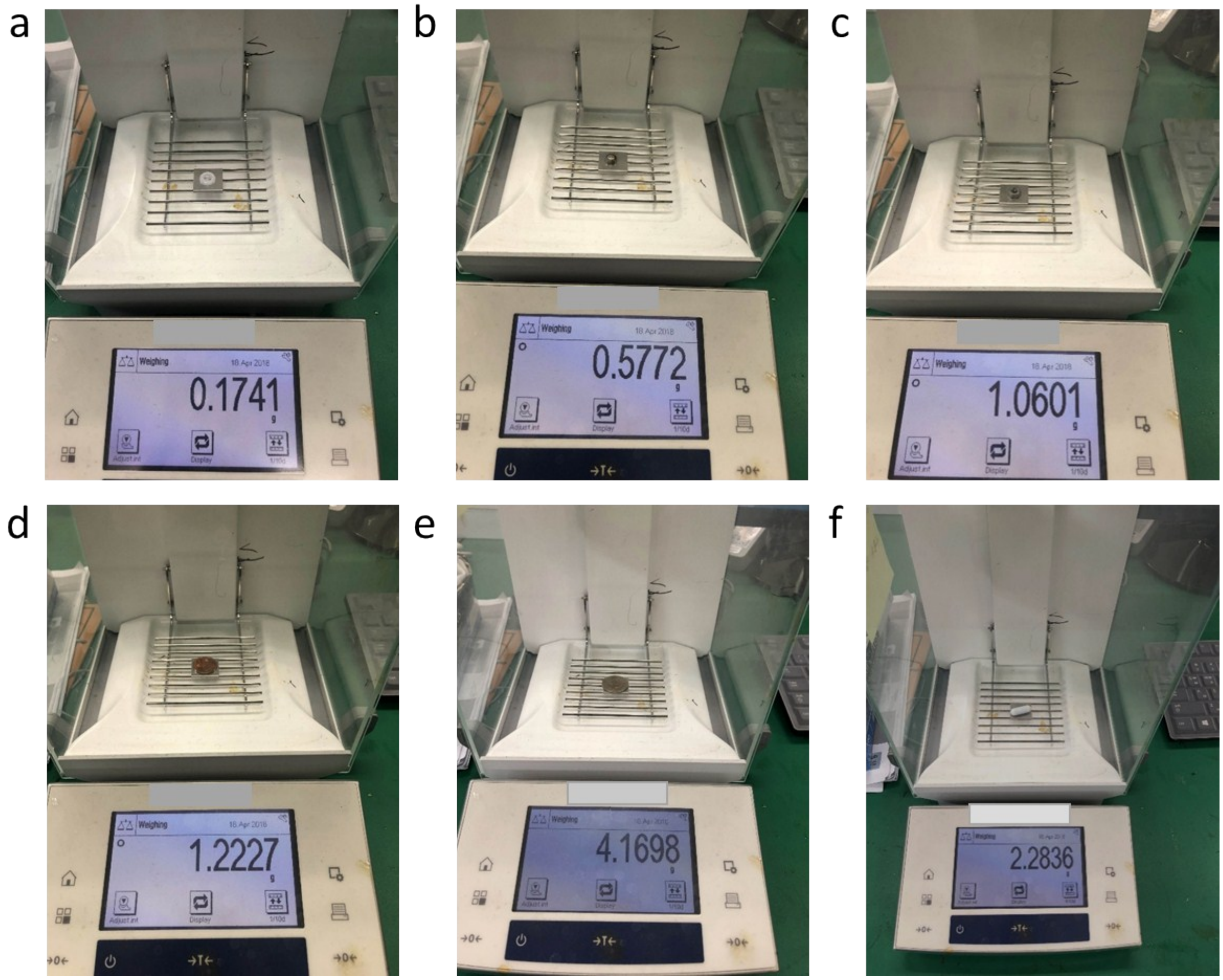

Figure S8 Weight of the small objects being measured in our experiments: a, cloth button; b, button cell; c, screw; d, 10 cent Korean coin; e, 50 cent Korean coin; f, 2cm magnetic bar.

Details of the objects:

a, Cloth Button: diameter: 11.196 mm; thickness: 1.791 mm; weight: 0.1741 g

b, Button Cell: diameter: 7.903 mm; thickness: 3.596 mm; weight: 0.5772 g

c, Screw: diameter: 7.824 mm; thickness: 3.833 mm; weight: 1.0601 g

d, 10 cent Korean Coin: diameter: 17.998 mm; thickness: 1.282 mm; weight: 1.2227 g

e, 50 cent Korean Coin: diameter: 21.608 mm; thickness: 1.424 mm; weight: 4.1698 g

f, 2cm Magnetic Bar: diameter: 7.118 mm; length: 1.996 mm; weight: 2.2836 g

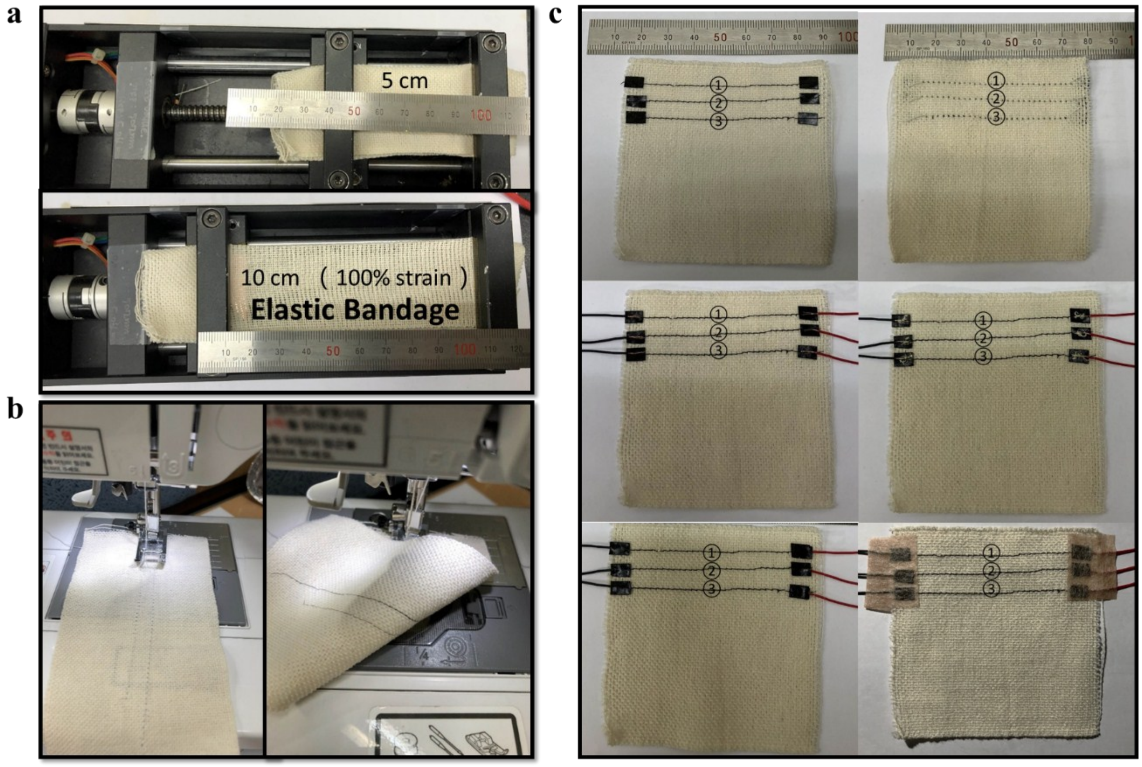

Figure S9 Fabrication of the wearable strain sensor.

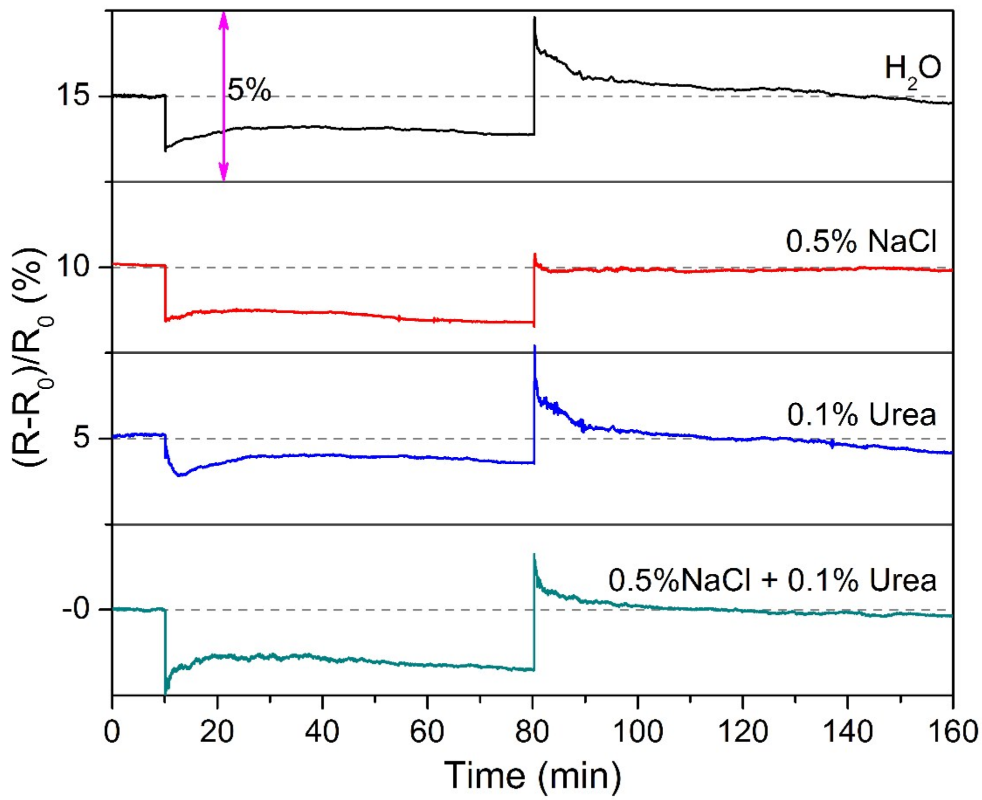

Figure S10 Relative change in resistance of MWCNT/TPU fiber based strain sensor in water and different artificial sweats.