Ultrasensitive and Highly Compressible Piezoresistive Sensor Based on Polyurethane Sponge Coated with a Cracked Cellulose Nanofibril/Silver Nanowire Layer

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Supporting Information

ABSTRACT: With the rapid development of flexible wearable electronics, a piezoresistive sensor with low detection limit and wide strain sensing range turns out to be a great challenge for its application in this field. Here, a cracked cellulose nanofibril/silver nanowire (CA) layer-coated polyurethane (PU) sponge was acquired through a simple dip-coating process followed by precompression treatment. The electrical conductivity and mechanical property of the conductive CA@PU sponge could be effectively tuned through changing the dip-coating number. As a piezoresistive sensor, the sponge exhibited the capability of detecting both small and large motions over a wide compression strain range of 0–80%. Based on the “contact effect”, the sensor possessed a detection limit as low as 0.2% and the gauge factor \(GF = (\Delta R/R_0)/\varepsilon\), where \(\Delta R\), \(R_0\), and \(\varepsilon\) represent the instantaneous resistance change, original resistance, and strain applied, respectively, was as high as 26.07 in the strain range of 0–6.6%. Moreover, the “contact effect” enabled the sensor to be applicable for larger strain, and the GF decreased first and then became stable with increasing compression strain. In addition, frequency- and strain-dependent sensing performances were observed, demonstrating that the sensor can respond reliably to different applied frequencies and strains. Furthermore, the sensor displayed exceptional stability, repeatability, and durability over 500 cycles. Finally, the sensor could be applicable for the detection of various human bodily motions, such as phonation, stamping, knee bending, and wrist bending. Most importantly, the sponge also exhibited great potential for the fabrication of artificial electronic skin. Herein, the conductive CA@PU sponge will undoubtedly promote the development of high-performance flexible wearable electronics.

KEYWORDS: PU sponge, silver nanowire, crack, ultrasensitive, piezoresistive sensor

1. INTRODUCTION

Owing to the drawbacks (e.g., limited strain detection range, rigidity, and complex fabrication process) of conventional metal and inorganic semiconductor-based sensors, high-performance flexible sensors have become a research hotspot with the rapid increase of flexible electronic industry, especially in the fields of electronic skin, human–machine interfaces, human health monitoring, speech recognition systems, and so forth. Currently, a variety of pressure sensors were designed according to different sensing mechanisms, including capacitive sensing, piezoelectric sensing, triboelectric sensing, and resistive sensing. Among them, a piezoresistive sensor, which converts external compressive pressure or strain into electrical resistance variation signal, has received great attentions because of its advantages of easy processing, simple structure, and low cost.

An electrical conductive polymer nanocomposite (ECPC), obtained from the combination of electrical conductive filler with a polymer matrix through suitable processing technology, has turned out to be intriguing candidates for a high-performance piezoresistive sensor. Its working principle...
Figure 1. Schematic illustration for the preparation of conductive CA@PU sponge.

is mainly based on the deformation of ECPCs that induced the rearrangement of the conductive network upon external compressive pressure or strain, causing the variation of electrical resistance.\(^{48-50}\) Especially, lightweight porous ECPC-based piezoresistive sensors provided an effective solution for the defect of small-strain detection range of conventional ones. Because of the high porosity and good elasticity of the polymer matrix, the “contact effect” between adjacent porous skeletons generated significant resistance variation signal over a wide strain range.\(^{41,51,52}\) Recently, our group has successfully fabricated porous carbon nanotube/thermoplastic polyurethane (TPU)\(^{53}\) and graphene/TPU\(^{54}\) nanocomposites using the environment-friendly freeze-drying technique, displaying excellent piezoresistive sensing behaviors with excellent reproducibility and recoverability over 90% compression strain. In addition, commercial sponges were also proved to be an ideal substrate to prepare porous piezoresistive sensor through a simple dip-coating technique.\(^{54,55}\) For instance, porous sea sponge was immersed into graphene and silver nanowire (AgNW) hybrid suspension, leaving conductive layer on the sponge skeleton after drying.\(^{56}\) The as-prepared piezoresistive sensor exhibited high sensitivity over a detection range of 50% compression strain. However, the “contact effect” usually occurred under higher strain for these porous ECPCs discussed above, resulting a bad detectability toward small strain and limiting their special applications, such as artificial skin.

To obtain porous ECPCs with good detectability for both small and large strains simultaneously, a rational microstructure design appeared to be an effective method for fabricating innovative porous ECPC-based piezoresistive sensors.\(^{57,58}\) Recently, ECPCs with a special microrack structure have shown a very positive role for enhancing their sensitivity and detectability in the small-strain region based on the open and closure of the cracks.\(^{57}\) For example, Wu et al. adopted an ion sputtering technique to fabricate conductive gold-coated PU sponge, and tunable crack densities were acquired through different precompression strains.\(^{52}\) As a result, the conductive sponge possessed a low detection limit (0.5% strain), wide sensing range (55% strain), and good reproducibility. Meanwhile, graphene-coated PU sponge with a fractured fiber network was obtained through the hydrothermal treatment and precompression process, and a low-pressure detection limit of 9 Pa was successfully achieved.\(^{59}\) However, the preparation processes of the samples stated above are complicated, which severely limit their large-scale production as piezoresistive sensors.

In this study, conductive cellulose nanofibril (CNF)/AgNWs (CA)-coated PU (CA@PU) sponge was fabricated using a simple dip-coating technique. Based on the high modulus of cellulose,\(^{50}\) the brittle conductive CA layer was easy to be fractured upon external compression, constructing a cracked structure easily. In addition, the application of CNF was also beneficial for the dispersion of AgNWs and the good adhesion between the conductive layer and PU skeleton. The microstructure of the conductive CA@PU sponge was investigated using a scanning electron microscope (SEM), and the compression mechanical properties were also studied. Most importantly, the piezoresistive sensing performance of the conductive CA@PU sponge under small and large compression strains was systematically tested to verify its detection limit and sensing range. Finally, the piezoresistive sensor was applied to detect human bodily motion with different strains, and a CA@PU artificial electronic skin was also designed to illustrate its broad application prospect.

2. EXPERIMENTAL SECTION

2.1. Materials. Commercial PU sponge with a density of 25 kg/m\(^3\) was purchased from Jiangxi Hongsiyuan Special Foam Material Co., Ltd. CNF aqueous dispersion with a solid content of 1 wt % was bought from Guilin Qihong Technology Co., Ltd. Dopamine hydrochloride (DA) and tris(hydroxymethyl-amino-methane) (Tris) were purchased from Shanghai Macklin Biochemical Co., Ltd. Silver nitrate (AgNO\(_3\)) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. Poly(vinylpyrrolidone) (PVP, \(M_w = 130 000 \text{ g mol}^{-1}\)) was obtained from Usolf Chemical Technology Co., Ltd, Tsingtao, China. Sodium chloride (NaCl) was bought from Zhiyuan Reagent Co., Ltd, Tianjin, China. Ethylene glycol (EG), ethyl alcohol, and acetone were supplied by Tianjin Fuyu Fine Chemical Co., Ltd, Tianjin, China. All of the materials and chemicals were used as received.

2.2. Preparation of AgNWs. AgNWs used in this experiment were synthesized through a modified polyelectrolyte technique.\(^{51,60}\) Briefly, 60 mL of PVP/EG solution (0.18 mol/L) and 30 \(\mu\text{L}\) of NaCl aqueous solution (0.1 mol/L) were first added into a three-necked flask and preheated at 170 °C in an oil bath for 90 min under stirring. Subsequently, 30 mL of freshly prepared AgNO\(_3\)/EG solution (0.12 mol/L) was added dropwise to the three-necked flask under stirring and heated at 170 °C for another 2.5 h. After reaction, the solution turned to be gray with a silky texture and cooled to room temperature. Then, the solution was added with a large amount of acetone and centrifuged (5000 rpm/min, 10 min) three times to purify the AgNWs. Finally, AgNWs were washed with ethanol three times to
remove excess EG and PVP and redispersed in water, and the mass loading of the as-prepared AgNWs dispersion was fixed as 10 mg/mL for the following application.

2.3. Fabrication of Conductive CA@PU Sponge. As shown in Figure 1, the conductive CA@PU sponge was prepared using a simple dip-coating technique. Briefly, the commercial PU was first washed with acetone and then dipped into the DA/Tris buffer solution (PH ≈ 8.5) for 24 h at 30 °C to obtain the polydopamine (PDA)-modified PU sponge. The color of the PU sponge turned to be brown with the deposition of PDA. Next, the PDA-modified PU sponge was repeatedly dipped into the CA solution (2 mg/mL) with a mass ratio of 3:2 under ultrasonication for 10 min. Then, the excessive solution was squeezed out from the sponge followed by drying at 80 °C for 1 h, achieving a gray conductive CA@PU sponge. Here, the dipping number was labeled as \( x \), and the corresponding sample was denoted as CA@PU\(_x\).
2.4. Preparation of Piezoresistive Sensor and Electronic Skin. In this study, the prepared conductive CA@PU sponge was applied with a precompression treatment to produce cracked structure on the surface of sponge skeleton, during which the sponge was first compressed to a strain of 80% at a rate of 5 mm/min and then returned to the initial state using a universal mechanical tester. For the piezoresistor sensor, conductive silver paste was applied to the two opposite faces of the cubic conductive CA@PU sponge (2 × 2 × 2 cm$^3$) to eliminate contact resistance and to collect stable resistance signal output. Then, conductive tapes were adhered to the two faces for resistance and piezoresistive sensing test. As for electronic skin, cubic conductive CA@PU sponges (1 × 1 × 1 cm$^3$) were used to construct 5 pixel × 5 pixel arrays on an insulating plastic plate. The surface and bottom of each sponge were coated with conductive silver paste, and then each row selection and each column selection were connected by a conductive tape.

2.5. Characterization. The micromorphology of sponge and AgNWs was observed through SEM (Zeiss MERLIN Compact) at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) was performed with a Tecnai G2 20 instrument at an acceleration voltage of 90 kV. X-ray diffraction (XRD) scans in the range of 10–100° were recorded using a Bruker-AXS D8 ADVANCE (Shimadzu Co. Ltd, XRD-6100) with Ni-filtered Cu Kα radiation (λ = 0.15418 nm) at a swing speed of 0.02°/min at 40 kV. The Fourier transform infrared spectroscopy (FTIR) spectrum in the range of 50–4000 cm$^{-1}$ was collected on a Nicolet NEXUS 870 instrument at a resolution of 4 cm$^{-1}$ using the attenuated total reflection mode. UV-vis absorption spectroscopy was performed on a UV-vis spectrophotometer (Agilent, Cary 5000) in the range from 300 to 700 nm. Cubic CA@PU sponges (2 × 2 × 2 cm$^3$) were subjected to a universal testing machine (Shimadzu, Japan) at a compression rate of 5 mm/min to investigate their compression performance. The I–V curves of the piezoresistive sensors were measured by an RST5000 electrochemical workstation (Suzhou Risetest Electronic Co., Ltd, China) with linear sweep voltammetry. The resistance of the piezoresistive sensor was tested using a digital multimeter (Tektronix DMM4050). Digital multimeter and universal tensile tester were used together to measure the piezoresistive sensing behavior of the sensor online.

3. RESULTS AND DISCUSSION

3.1. Characterizations of AgNWs. SEM and TEM were conducted to study the morphology of the prepared AgNWs. As shown in Figure 2a, AgNWs with an average length of 20–30 μm were obtained with very few silver nanoparticles, showing the high purity of AgNWs. The TEM image (see Figure 2b) displayed the diameter of AgNWs which is about 150 nm. Besides, about 3 nm thick PVP identified through FTIR (see Figure S1) was observed on the surface of AgNWs.63 It is well known that the existence of PVP can effectively prevent the oxidation of AgNWs and improve the dispersity of AgNWs in water.64 To further demonstrate the purity and the structure of AgNWs, UV–vis spectra (see Figure 2c) and XRD spectra (see Figure 2d) of AgNWs were characterized. Generally, the existence of the absorption peaks at 350/390 and 410 nm in the UV–vis spectrum is the characteristic peaks of long AgNWs and silver nanoparticles, respectively.65,66 Hence, the absence of the absorption peak at 410 nm in Figure 2c also verified the high purity of the prepared AgNWs. As for the XRD spectrum of AgNWs, five characteristic diffraction peaks were observed at 2θ = 38.06, 44.26, 64.4, 77.34, and 81.48°, corresponding to the (111), (200), (220), (311), and (222) crystalline planes of pure face-centered cubic silver crystals, respectively.63

3.2. Characterizations of Conductive CA@PU Sponge. As shown in Figure 3a–e, the commercial PU sponge possessed an interconnected 3D porous structure with a pore diameter of 300–500 μm and smooth skeleton. After the self-polymerization of PDA, there was almost no obvious change about the interconnected 3D porous structure (see Figure 3d), but the surface of the sponge skeleton becomes rough because of the existence of wrinkled PDA layer (see Figure 3e). Here, PDA was applied to improve the hydrophilicity of PU sponge to facilitate the dip-coating process in the next step.67 This can be verified from Figure S2 that the water contact angle (WCA)
of the PU sponge decreased from 141° to 84°, indicating the transformation of PU sponge from hydrophobicity into hydrophilicity. Therefore, it can be clearly seen in Figure 3j that both the outer and fracture surfaces presented uniform gray in color, indicating that the CA solution can easily permeate into the porous structure. Meanwhile, the excellent adhesion of PDA can also enhance the adhesion strength between CA layer and PU skeleton.67 After cyclic dip-coating in CA solution, the conductive CA@PU sponge also inherited the interconnected 3D porous structure of PU (see Figure 3g), but the roughness of the surface of the porous skeleton was further increased because of the homogeneous distribution of AgNWs (see Figure 3h). Besides, as expected, a cracked CA conductive layer was successfully constructed on the sponge skeleton (Figure 3i). Finally, a green leaf could support the conductive CA@PU sponge without being bent (see Figure 3k), indicating that the lightweight characteristic of PU sponge was well maintained.

3.3. Mechanical Property of Conductive CA@PU Sponge. Generally, good mechanical property is crucial for an ideal piezoresistive sensor. Here, a series of compression tests were conducted at a compression rate of 5 mm/min to study the mechanical property of PU sponge and different CA@PU sponges. As shown in Figure 4a, three typical distinct stages were observed for the compressive stress–strain curves of PU sponge:66 the linear elastic region for $\varepsilon < 10\%$ within which the stress increased quickly and linearly; the plateau region for $10\% < \varepsilon < 60\%$ within which the stress increased slowly; and the densification region for $\varepsilon > 60\%$ within which the stress increased sharply. Besides, it can be clearly seen that the stress can almost completely return to the initial point for each strain when the PU sponge was unloaded, and very small residual strain was observed even for large strains of 60% and 80% (Figure S3). All of these indicated the excellent elasticity of AgNWs.60 The conductive CA@PU sponge was subjected to cyclic compression test under 40% strain at a compression rate of 5 mm/min, and the typical compressive stress–strain curves for the first and 500th cycles are displayed in Figure 4d. Compared with the hysteresis loop of the first cycle, a shrinkage of the hysteresis loop was observed for the 500th cycle and the maximum stress decreased from 5.8 to 4.6 kPa at the 40% strain. It indicated the excellent mechanical fatigue resisting performance of the CA@PU sponge. Meanwhile, there was still no residual strain after 500 cycles, showing excellent compressibility and recoverability. All of these are very important for the durability and reproductivity of ideal piezoresistive sensor.

3.4. Electrical Property of Conductive CA@PU Sponge. As shown in Figure 5a, the electrical conductivity and the CA loading of conductive CA@PU sponge as a function of dip-coating number were investigated. Observably, the conductivity increased sharply from $1 \times 10^{-13}$ to $1.3 \times 10^{-4}$ S/cm after coating 12 times, indicating that the conductive network had reached the conductive region for $\varepsilon < 60\%$ within which the stress increased quickly and linearly; the plateau region for $10\% < \varepsilon < 60\%$ within which the stress increased slowly; and the densification region for $\varepsilon > 60\%$ within which the stress increased sharply. Besides, it can be clearly seen that the stress can almost completely return to the initial point for each strain when the PU sponge was unloaded, and very small residual strain was observed even for large strains of 60% and 80% (Figure S3). All of these indicated the excellent elasticity of AgNWs.60 The conductive CA@PU sponge was subjected to cyclic compression test under 40% strain at a compression rate of 5 mm/min, and the typical compressive stress–strain curves for the first and 500th cycles are displayed in Figure 4d. Compared with the hysteresis loop of the first cycle, a shrinkage of the hysteresis loop was observed for the 500th cycle and the maximum stress decreased from 5.8 to 4.6 kPa at the 40% strain. It indicated the excellent mechanical fatigue resisting performance of the CA@PU sponge. Meanwhile, there was still no residual strain after 500 cycles, showing excellent compressibility and recoverability. All of these are very important for the durability and reproductivity of ideal piezoresistive sensor.

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Conductive networks were established with increasing CA loading. Hence, the electrical property of the CA@PU sponge could be effectively tuned through changing the coating number. In addition, the $I$–$V$ curves of different conductive CA@PU sponges were tested and are displayed in Figure 5b. All of the samples exhibited good linear ohmic behaviors, indicating good stability of the electrical property. This is very important for the sensor to perform stable sensing behavior. Finally, the conductive CA@PU sponge was connected with a blue light-emitting diode (LED) to visualize the piezoresistive effect of the sponge. It can be clearly observed that the brightness of the LED became stronger upon external compression strain and dimmed after releasing strain (see Figure 5c and Video S1). All of these indicated the great potential of as-prepared CA@PU sponge to serve as a piezoresistive sensor.

### 3.5. Piezoresistive Property of Conductive CA@PU Sponge

**Figure 6.** (a) $\Delta R/R_0$ of conductive CA@PU$_{24}$ sponge with increasing compression strain; (b) enlarged picture of the rectangle part in (a); and (c) schematic evolutions of the porous structure with increasing compression strain.

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each compression cycle, based on the “crack effect” in the small-strain range, the resistance was increased linearly by about 3.6, 9.24, and 18.7% toward 0.2, 0.4, and 0.6% strain, respectively (Figure 7a). Meanwhile, the resistance was decreased by about 33.7, 87.9, 95.1, and 98.6% toward 4, 40, 60, and 80% strain because of the “contact effect” (Figure 7b) in the large strain range, respectively. After releasing the strain, because of the excellent compression-resilience properties of the sponge, the resistance almost fully recovered to its initial value for both small and large strain ranges, showing excellent recoverability. Importantly, the sensor also displayed stable repeatability under different compression strains, which is very crucial for its practical applications. Notably, a compressive strain as low as 0.2% could be effectively detected, endowing the sensor with the capability of discerning small motion, such as pulse, heart monitoring, and speech. To detect the durability
of the sensor, the piezoresistive behavior under 40% strain during 500 cycles was conducted. As displayed in Figure 7c, the response pattern kept almost unchanged in each cycle. The resistance of the sensor increased first due to the open of cracks and then decreased arising from the contact of the skeleton of PU sponge upon external compression. After releasing the compression strain, the resistance completely restored to its initial value based on the recovery of the conductive network. All these are ascribed to the stable compression mechanical property of the sponge. Finally, the frequency dependence of the piezoresistive behavior of the sponge was evaluated, and an increase trend in sensitivity with increasing frequency was observed (Figure 7d). The frequency-dependent piezoresistive behavior will undoubtly enhance the discernibility of the piezoresistive sensor.

3.6. Applications in Human Motion Detection. As discussed above, the piezoresistive sensor possesses high sensitivity toward small and large strains. To disclose its feasibility in the wearable electronic device, a series of tests were conducted to detect different human motions. First, the sensor was adhered to the throat using a medical waterproof tape to detect the small motion caused by phonation (Figure 8a). As a result, significant resistance variation was accurately recorded because of the small compression and release induced by the throat when the tester made a sound. Besides, the sensor also exhibited excellent stability and repeatability upon repeated pronunciation. Hence, the sponge sensor possessed great potential to act as a voice recognition device. As for the large-scale motions, the sensor was fixed to the sole of the shoe to detect the stamping. As expected, the sensor displayed sharp and repeatable resistance variation signal upon consecutive stamping (Figure 8b), which impose great compression to the sensor. Meanwhile, the sensor was attached onto the knee and wrist to detect their movements. Obviously, the sponge also demonstrated outstanding stable and reproducible response patterns upon the bending of knee and wrist (Figure 8c,d). All of these indicated that the piezoresistive sensor possesses great potential in the fields of human health and sports monitoring.

3.7. Electronic Skin. Based on the excellent compressibility and piezoresistive performance of the conductive CA@PU sponge, cubic samples were integrated into 5 × 5 pixels to investigate its potential applications in a compression-sensitive artificial electronic skin (Figure 9a). The schematic diagram of the artificial electronic skin is illustrated in Figure 9d. The color contrast mapped with external applied pressure according to the resistance variation ratio of each pixel was plotted. As shown in Figure 9b, a 100 g weight was placed onto the surface of the artificial electronic skin; it can be obviously observed the significant difference of resistance variation ratio based on the different applied pressures at different locations. Meanwhile, the corresponding resistance variation ratio in Figure 9e is consistent with the location and shape of the weight. Similarly, as shown in Figure 9c, a stone ball located on the surface of artificial electronic skin could also be accurately monitored through the color contrast map in Figure 9f. The results demonstrated the great potential of the CA@PU sponge-based artificial electronic skin to detect the location and shape of the external object. To fulfill the scale production of the CA@PU sponge-based artificial electronic skin in the future, the precise control of the precompression process that produce the ultrasensitive crack structure is very crucial. In addition, advanced technique such as the photolithography technique could be applied to fabricate electronic skins with more pixels, which will be helpful for the improvement of the resolution of CA@PU electronic skin.

4. CONCLUSIONS

In summary, a conductive CA@PU sponge was successfully prepared through repeatedly dipping the PU sponge into CNF/AgNW solution. It is noted that the mechanical and electrical properties of the conductive CA@PU sponge could be adjusted by changing the dip-coating number. With the increase of dip-coating number, both of the compressive strength and compressive modulus of the sponge increased due to the high modulus of cellulose and the rigidity of AgNWs. Meanwhile, the electrical conductivity was also enhanced based on the progressive construction of effective conductive networks. As a piezoresistive sensor, a cracked structure was effectively constructed in the conductive CA layer through a precompression strain up to 80% at a rate of 5 mm/min. Hence, the conductive CA@PU sponge exhibited a detection limit as low as 0.2% and an ultrahigh GF of 26.07 based on the “crack effect” for small strain. In addition, it also displayed exceptional stability, repeatability, and durability for a larger compression strain up to 80% because of the “contact effect”. All of these excellent sensing characteristics made it applicable
for the detection of various human bodily motions, such as phonation, stamping, knee bending, and wrist bending. Most importantly, the sponge also exhibited great potential for the fabrication of artificial electronic skin. We believe that this simple design will undoubtedly promote the development of high-performance flexible wearable electronics.

**ASSOCIATED CONTENT**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b00900.

FTIR spectra of as-prepared AgNWs and PVP; WCA of original PU sponge and PDA-treated PU sponge; residual strain of the PU sponge after 60 and 80% compression strains; and compressive stress-strain curves of CA@PU6 sponge and CA@PU12 sponge under different strains (PDF)

Light intensity of the LED connected with the conductive CA@PU sponge changed with the compression and release of strain (AVI)

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**Notes**

The authors declare no competing financial interest.

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