Intrinsic elastic conductors with internal buckled electron pathway for flexible electromagnetic interference shielding and tumor ablation

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ABSTRACT The elastic conductor is crucial in wearable electronics and soft robotics. The ideal intrinsic elastic bulk conductors show uniform three-dimensional conductive networks and stable resistance during large stretch. A challenge is that the variation of resistance is high under deformation due to disconnection of conductive pathway for bulk elastic conductors. Our strategy is to introduce buckled structure into the conductive network, by self-assembly of a carbon nanotube layer on the interconnecting micropore surface of a pre-strained foam, followed by strain relaxation. Both unfolding of buckles and flattening of micropores contributed to the stability of the resistance under deformation (2.0% resistance variation under 70% strain). Microstructural analysis and finite element analysis illustrated different patterns of two-dimensional buckling structures could be obtained due to the imperfections in the conductive layer. Applications as all-directional interconnects, stretchable electromagnetic interference shielding and electrothermal tumor ablation were demonstrated.

Keywords: intrinsic elastic conductor, buckled structure, three-dimensional conductive network, electromagnetic interference shielding, electrothermal tumor ablation

INTRODUCTION

Stretchable electronic devices have been attractive for applications in soft robotics and wearable healthcare monitoring [1–3]. Elastic conductors play a key role in

interconnecting these devices, or work as their electrodes, which can be divided into intrinsic and structural conductors. In general, conductive materials (such as metal nanowires and carbon-based nanomaterials) are rigid and non-stretchable, while soft elastomeric materials (such as polydimethylsiloxane (PDMS) and polyurethane (PU) sponge) are non-conductive. The fabrication of stretchable conductors has been realized successfully by combining conductive materials with soft substrates. However, such stretchable conductors did not have high stretchability, uniform bulk structure, and stable conductance. Therefore, intrinsic elastic conductors with high stretchability and small resistance change in low cost and easy processing are highly desirable in stretchable electronics, whereas they have not been developed yet.

The intrinsic conductors, such as solid metal/carbon filler elastomer composites [4,5], conductive copolymers or composites [6,7], and liquid metal (LM) composites [8,9], show stretchability and conductivity. One efficient method is to disperse a conductive material into an elastic matrix to form a conductive network. For example, Baik's group [10] prepared a hybrid elastic film based on silver flakes and multi-walled carbon nanotubes (MWCNTs), and Takao's group [11] mixed silver flakes with fluorine rubber using fluorine surfactant to obtain good dispersion. Ko's group [12,13] demonstrated a highly stretchable and transparent conductor by embedding Ag nanowire percolation network on a PDMS film for elec-

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tromagnetic interference (EMI) shielding and heating. Similarly, Bao's group [14,15] prepared conductive polymer-based intrinsic conductors by mixing poly(3,4-ethylenedioxythiophene) with elastomers or by copolymerization. These intrinsic elastic conductors show bulk structures and high conductivities, but the resistance change is high due to the decreased contact between the conductance pathway under stretching.

As an alternative, structural conductors show stable resistance change during stretch by use of buckled or serpentine structural design for rigid conductors [16–19]. Such structures are generally prepared by attaching the conductive thin layer on a pre-stretched elastomer substrate followed by stretch-release, or using digital mechanical cutter plotter. A wide range of materials have been used as the conductive layer, including metal nanowires [20,21], CNTs [22,23], and conductive polymers [24]. However, it is not feasible for the bi-layered structure to improve the conductivity by simply increasing the thickness of the conductive layer, because a thick, high-modulus top layer can hardly buckle on a low-modulus elastic substrate. When releasing the pre-strain, a soft elastic substrate would produce a compress strain on the top layer, whereas the compress strain is not enough to form the buckle in a thick, rigid conductive layer. Moreover, this bi-layered structure is difficult to use when an all-directional interconnect or a uniform bulk structure is required, such as in EMI shielding and radar wave absorption [25]. In our previous work [26], a layer-

by-layer technique was used to prepare a multi-layer, buckled elastic conductor, which increased the conductivity while maintaining the resistance stability under deformation. However, this structure did not show conductivity in the thickness direction, and the preparation required complicate iterative coating-stretching processes. As such, it is still a challenge to obtain a bulk elastic conductor with constant resistance during deformation.

One possible solution is to introduce micron- or nano-scale buckled structures in the three-dimensional (3D) conductive network of the intrinsic conductors without using a substrate (Fig. 1a). A hot-pressing process can produce the buckled structure in the foam; when the conductive networks are partially broken during stretch, the resulting elastic conductor still shows a high resistance change (>20 times resistance increase for 150% strain) [27]. To the best of our knowledge, this proposed configuration for obtaining stable resistance change has not yet been reported. In this paper, we successfully introduced the buckled structure into an intrinsic elastic conductor, using polypropylene (PP) foam as an elastic matrix and single-walled CNTs (SWCNTs) as the conductive phase. SWCNT formed a 3D network by self-assembly on the interconnecting pore surface of a pre-stretched PP foam; releasing the pre-stretch resulted in buckling of the SWCNT network. The resulting buckled SWCNT/PP foam showed 2.0% resistance change upon stretching for 70% strain, corresponding to a quality

Figure 1 Structures of the intrinsic conductor with buckled 3D network. (a) Schematic demonstrations showing that (top) the buckled 3D conductive network in an intrinsic elastic conductor keeps intact during stretching, (middle) the 3D conductive network without buckled structure in an intrinsic elastic conductor disconnects during stretching, and (bottom) the elastic conductor with a buckled conductive surface layer keeps intact during stretching. (b) Optical photographs showing that the BSPF₁ is stretched, bent, cut and folded into different shapes, indicating its excellent flexibility. (c) Optical photographs showing a piece of BSPF₁ supported on the petal of a primula flower, indicating its light weight. (d) Low and high resolution SEM images for biaxial BSPF₃, observed from the surface and the cross-section. The BSPF_m in (b) to (d) were prepared by using biaxial strain of 35%.

factor ($Q = (\Delta R/R_0)/(\Delta L/L_0)$). ΔR and R_0 represent the resistance change and initial resistance of the sample; ΔL and L_0 represent the length change and initial length) of 0.028, which is much lower than those of other state-of-the-art intrinsic conductors. We also showed their potential applications in all-directional electrical interconnects, EMI shielding, and tumor ablation.

EXPERIMENTAL SECTION

Fabrication of the SWCNT/PVP ink

SWCNTs (average length of $\sim 5\ \mu\text{m}$ and diameter of 1.6 nm, OCSiAl TUBALL^{TM} Co. Ltd.) was mixed with sodium dodecyl sulfate (SDS, 0.1 wt%, Sigma-Aldrich Co.) in deionized water and dispersed with high-shear mixing (Cat: X120), followed by sufficient sonification to ensure dispersion of SWCNTs in water. Polyvinylpyrrolidone (PVP, Lot no.P48497-500g, Beijing Innochem Science Technology Co. Ltd.) was then added, followed by 12 h sonification at 50°C [28]. The weight percents of the SWCNT and PVP are 0.2% and 0.4%, respectively.

Fabrication of BSPF_m

The PP foam with a thickness of 150 μm purchased from Nitto Denko Co. Ltd. (Model 0924512) was pre-stretched uni-axially or bi-axially to different strains and fixed on a home-made frame with the use of parafilm. It was then immersed in the SWCNT/PVP ink for 10 min, and then dried at 50°C in an oven for 5 min to evaporate water. The above processes were repeated for a certain number of cycles to increase the SWCNT loading, and then the composite foam was relaxed from the frame to form BSPF_m (m represents the number of cycles repeated). If not specified, the frame used for biaxial stretch had a dimension of 6 cm $\times$ 6 cm, and the frame used for uni-axial stretch had a dimension of 4 cm $\times$ 9 cm.

Characterizations

Raman spectra were conducted on a Labram spectrometer (SR-500I-A) with laser wavelength of 532 nm. The scanning electron microscopy (SEM) images were taken on a field emission scanning electron microscope (MERLIN Compact). The transmission electron microscopy (TEM) images were obtained on a transmission electron microscope (model JEM-2800). The SEM images were obtained as follows. First, the BSPF₁ was stretched to different strains (0%, 30%, and 50%), the both ends were fixed by using copper wires, and the SEM images were obtained by attaching the BSPF₁ vertically on the silicon

wafer to expose the cross-section of the foam to the electron beam. It should be emphasized that these SEM images at different strains originated from the same position. The electrical resistances of the samples were measured on a Keithley SourceMeter (2400) using a four-probe configuration. The electrical resistance measurements were repeated for five times to obtain the average value. The mechanical properties were obtained on an Instron mechanical tester (model 3365), with a 5 N load cell and at a stretch rate of 60 mm min⁻¹. The stress and strain were engineering values. The contents of SWCNT in BSPF_m were obtained by thermogravimetric analysis (TGA) on a thermogravimetric analyzer (model TGA/DSC1), under air atmosphere at a heating rate of 10°C min⁻¹ from room temperature to 600°C. Thermal infrared (IR) images and temperature were obtained on an infrared thermometer (FLIR T440). The EMI shielding effectiveness (SE) was obtained on a vector network analyzer (model Agilent N5242A) in a frequency range of 8–12 GHz. The sample size was 22.5 mm $\times$ 10.0 mm $\times$ 2 mm. Micro computed tomography was carried out on Cytovia (model HSI 3D Plus).

RESULTS AND DISCUSSION

Fabrication and morphology of buckled SWCNT/PP foam

The SWCNTs used in this work had an average diameter of 1.6 nm and a length of 5 μm (aspect ratio >3000), so it showed a high flexibility. The Raman spectra of SWCNTs showed a high G-band peak at 1590 cm⁻¹ and a small D-band peak at 1330 cm⁻¹ (Fig. S1a), indicating a highly graphitic structure. The SWCNTs (0.2 wt%) were dispersed in water by using SDS (0.1 wt%) and PVP (0.4 wt%) as dispersants [28], which formed a highly sticky ink and did not show sedimentation for over three months (Fig. S1b). The TEM images showed the coating of SWCNTs by PVP chains (Figs S3 and S4). The PP foam used in this paper contained 90% porosity with interconnecting pores with an average pore size of 24 μm (Figs S5 and S6a). The large porosity and interconnecting pores enabled effective penetration of CNTs inside the foam. On the other hand, the pore size and distribution also affected the stretchability of the PP foam. Increasing pore size or distribution could share more applied strain under the foam, which is beneficial to stabilizing the deformation. The PP foam showed good hydrophilicity (Fig. S6b and Movie S1), enabling the wetting of SWCNT/PVP water dispersion and conductive network formation upon drying.

Dipping the PP foam directly in SWCNT dispersion for

10 min, followed by drying in an oven at 50°C for 5 min to evaporate the water, made the CNTs form an inter-connecting conductive network. Such a conductive network did not contain the internal buckled structure, so the PP foam was pre-stretched before being dipped into the SWCNT dispersion in the following experiments. This PP foam can be reversibly extended to as large as 35% strain during the biaxial stretch or can be reversibly extended by up to 80% for uniaxial stretch. Consistent with the above method, releasing a biaxial pre-strain after drying out enabled the formation of buckles in the SWCNT conductive network (Fig. S2). But it should be noted that the foam swelled by 3% lateral strain by being dipped into the SWCNT dispersion for 10 min. The PP foam could recover the initial size when it was dried. SEM images showed the bi-directional buckled SWCNT layer on the pore surface inside the foam (Fig. 1d). The cross-sectional images indicated that no delamination of SWCNT occurred from the pore surface (Fig. S7). Micro computed tomography showed a 3D-connected network of conductive layer with buckled structure (Movie S2). Optical pictures showed that the buckled SWCNT/PP foam was light-weight and could stand on the petal of a primula flower (Fig. 1c). It could tolerate various mechanical deformations such as stretching and bending, and could be easily cut and folded into different shapes (Fig. 1b). Similarly, the uniaxial buckled SWCNT conductive network was also prepared by using uniaxial pre-stretch of PP foam.

It should be mentioned that, for biaxial pre-stretch, the same pre-strain in both directions were used (called fabrication strain, ε_{fab}). For increasing the conductivity, the pre-stretched foam was dip-coated with SWCNT ink and dried for seven cycles before the release of pre-strain, and BSPF_m was used to represent the buckled SWCNT/PP foam with m dip-coating cycles.

Electrical and mechanical properties of BSPF_m

In order to qualitatively test the all-directional bulk conductivity and stretchability of the BSPF_m, we connected the light emitting diodes (LEDs) from the top surface to the bottom surface, or to the side surface, or to the freshly-cut surface of the BSPF₁ (1.2-cm-thick) using copper wires, and the LEDs came to light (Fig. S8a–c). This indicates the bulk conductivity of BSPF_m. In addition, a 4-mm-thick BSPF₃ was used as a stretchable interconnect for a clock, by connecting the copper wires to its different surfaces. The clock worked well when the BSPF₃ was repeatedly stretched (Movie S3). We also connected six LEDs from the top and the bottom surfaces

of four pieces of BSPF₁, and attached them on the elbow of a person. The LEDs kept lighting up during the deformation of the elbow (Movie S4). Moreover, the brightness of the LEDs was negligibly changed by eye during various deformations such as twisting and coiling (Fig. S9).

In the following sections, we quantitatively investigated the electrical and mechanical properties of BSPF_m, and their dependencies on the fabrication strain and number of dip-coating cycles for biaxial and uniaxial pre-stretches. For obtaining repeatable characterization results, the BSPF_m was pre-stretched for ten cycles to the maximum available strain before electrical and mechanical tests. All the tests were performed in uni-directional stretch.

Fig. 2a shows the percent resistance change ($\Delta R/R_0$) as a function of strain for BSPF₁ with different fabrication strains. The resistance increased under stretching, and returned to the initial value during stretch-release. With the increase in the biaxial fabrication strain from 0% to 35%, the resistance change monotonically decreased from 15.1% to 3.8% for 70% uni-directional stretch. In more detail, a hysteresis in the reversible stretching test for a smaller biaxial fabrication strain was observed. This is because the buckle density increased with the increase in pre-strain (as shown from SEM images in Fig. S10), which prevents the conductive network from further stretching-based deformation and the increase in the resistance change for BSPF_m. Hence, the hysteresis for larger fabrication strain decreased due to the structural integrity of the CNT network during deformation. Uni-axial mechanical tests showed that the BSPF₁ can completely recover the initial mechanical properties five minutes after strain relaxation, indicating good mechanical reversibility (Fig. S11b).

The resistance per stretched length, R_ϵ/L_ϵ , also decreased with increasing fabrication strain (Fig. S11c), where R_ϵ and L_ϵ are the resistance and the length at strain (ϵ), respectively. This should be ascribed to the increased SWCNT content in BSPF_m with higher fabrication strain (Fig. S11a), where an increased pore surface area could be coated with SWCNTs. This result indicates that higher fabrication strain helps obtain higher conductivity for BSPF_m. Interestingly, the conductivity increased with increasing strain, corresponding to the decreased R_ϵ/L_ϵ at a higher strain level (Fig. S11d).

We then investigated the dependencies of electrical and mechanical properties on the number of dip-coating cycles for preparing the BSPF_m. With increasing m from one to seven, SWCNT contents increased and correspondingly the conductivity at the relaxed state increased from

Figure 2 Stability of resistance for BSPF_m at different applied strains. (a) $\Delta R/R_0$ as a function of the applied strain for BSPF₁ with different biaxial fabrication strains. (b) $\Delta R/R_0$ as a function of the applied strain for BSPF_m with m . (c, d) Comparison of (c) resistance change and (d) quality factor with maximum available strain for BSPF_m with previously reported typical 3D intrinsic stretchable bulk conductors. The filled and open symbols in (a) and (b) indicate loading and unloading processes, respectively.

5.2 to 60.6 S m⁻¹ (Fig. S12a–c). The resistance change increased from 3.8% to 6.3% while the maximum available strain decreased from 70% to 40% (Fig. 2b). This can be attributed to the increased rigidity of the conductive phase with increasing m (Fig. S13a, b). Fig. S14 shows that the distance between the buckles of the SWCNT layer increased with increasing m . More importantly, BSPF_m showed good mechanical reversibility within the maximum available strain for different m and multiple stretch-release cycles (Fig. S13c, d), which would facilitate their use as elastic interconnects.

In order to show the generality of this pre-stretch-based approach for buckle formation in intrinsic elastic conductors, we further investigated the BSPF_m with uniaxial fabrication strain. The uniaxial BSPF_m presented parallel buckled structures perpendicular to the pre-stretch direction, which showed increased a buckle density with increasing fabrication strain and decreased buckle period with increasing m (Figs S15 and S16). Similar dependencies of electrical and mechanical properties on strain were obtained for uniaxial BSPF_m with different fabrication strains and different numbers of dip-coating cycles (Fig. 3a and Figs S17–S19). For example, the resistance change decreased from 15.1% to 2.0% for uni-

axial BSPF₁ as the fabrication strain increased from 0% to 80%. It is interesting that even when stretched beyond the fabrication strain, the uniaxial BSPF_m still showed relatively stable resistance. For instance, stretching the uniaxial BSPF₁ with a fabrication strain of 50% to an applied strain of 70% only showed resistance change of 5.6% (Fig. 3a).

It is important for an intrinsic bulk conductor to show stable resistance when stretched in different directions. We then investigated the resistance change for stretching a biaxial BSPF₁ and a uniaxial BSPF₁ in different directions. Fig. 3c shows that no significant resistance difference was observed by stretching a biaxial BSPF₁ to 70% strain along each of the pre-strain axis (3.8%) or at 45° direction (3.4%) with the pre-strain axis. This resistance homogeneity in different axes is likely due to the fact that the bi-directional buckles in the SWCNT conducting network could accommodate deformations in different directions [29]. Different from the biaxial case, stretching the uniaxial BSPF₁ in the pre-strain direction showed smaller resistance change (2.0%) than along the 45° direction (3.6%) and in the perpendicular direction (5.5%) (Fig. 3b). Nevertheless, then uniaxial BSPF_m stretched in different directions was more stable than the SWCNT/PP

Figure 3 Electrical properties of BSPF_m for different types of deformations. (a) $\Delta R/R_0$ as a function of applied strain for BSPF₁ with different uniaxial fabrication strains. (b, c) $\Delta R/R_0$ as a function of applied strain for (b) uniaxial BSPF₁ and (c) biaxial BSPF₁ along different stretching directions. (d) $\Delta R/R_0$ at different stretching/releasing cycles for biaxial BSPF₁. The inset shows the $\Delta R/R_0$ as a function of applied strain for the 1st, 100th, and 500th cycles. (e) $\Delta R/R_0$ at different bending cycles for biaxial BSPF₁ with a bending radius of 2 mm. The left inset shows the $\Delta R/R_0$ as a function of bending radius, and the right inset shows an optical image of a BSPF₁ bending around an 8-mm-diameter mandrel. (f) $\Delta R/R_0$ for biaxial BSPF₁ as a function of applied compressive strain. The optical images from left to right in the inset show the BSPF₁ under 30% and 70% compressions, and after relaxing compression, respectively. The filled and open symbols indicate loading and unloading processes, respectively. The uniaxial fabrication strain in (b) was 80%, and the biaxial fabrication strain in (c–f) was 35%.

foam without buckled structure (15.1%). This indicates that BSPF_m is suitable for use as an intrinsic bulk conductor for different stretching directions.

To investigate the stability for long-term use, cycling tests were carried out on the biaxial BSPF_m for different types of deformations (Fig. 3d–f). The resistance negligibly changed by stretching the biaxial BSPF₁ to different strains for ten stretch/release cycles, and slightly increased to 4.3% after 500 cycles, with the resistance at unloading slightly increased by 0.3%. Bending the biaxial BSPF₁ down to 2-mm radius decreased the resistance by 0.16%, which negligibly changed for ten cycles. Compressing the biaxial BSPF₁ with 80% decrease in thickness resulted in a resistance change of 3.9%, which negligibly changed for ten cycles (Fig. S20). Similar cycling results were obtained for uniaxial BSPF₁ for stretching and bending deformations (Fig. S21).

Fig. 2c and d compare the percent resistance change and the quality factor Q as a function of the maximum available strain for the BSPF_m with previous reported 3D, bulk intrinsic elastic conductors [8,27,30–38], respectively. It can be seen that the uniaxial and biaxial BSPF_m

showed the lowest percent resistance change and quality factor among these intrinsic conductors. Even if the maximum available strain (70%) is not the highest number, it should meet the requirements for most cases of wearable electronic applications because this value is close to the maximum strain for person's movement (such as for elbow, ~75%) [39].

Microstructural analysis during deformation

In order to understand the mechanism of resistance stability during the deformation of the BSPF_m, we here discussed the buckle formation in the interconnecting SWCNT network, and its microstructural evolution under deformation. The SWCNT/PVP film showed good conductivity, mechanical flexibility and toughness, which can be deformed into various shapes (Fig. 4a and c). The SWCNT/PVP film showed negligible resistance change upon stretching to 6%. When coating on the pore surface of the PP foam, the SWCNT/PVP film formed an interconnecting conductive network inside the foam by self-assembly. An important point is that the SWCNT/PVP layer showed strong adhesion with the PP foam surface,

Figure 4 Optical images, electrical and mechanical properties of SWCNT/PVP film, SWCNT/PVP/VHB without pre-strain, SWCNT/PVP/VHB with uniaxial and biaxial fabrication strains. (a) Optical images from left to right were SWCNT/PVP film before and after bending, the SWCNT/PVP/VHB without pre-strain, the biaxial and uniaxial SWCNT/PVP/VHB. (b) $\Delta R/R_0$ as a function of applied strain for SWCNT/PVP film, SWCNT/PVP/VHB without pre-strain, SWCNT/PVP/VHB with biaxial fabrication strain of 35% and uniaxial fabrication strain of 80%, and BSPF₁ with biaxial fabrication strain of 35% and uniaxial fabrication strain of 80%. (c) Stress-strain curve for SWCNT/PVP film. (d) Electrical conductivity as a function of applied strain for SWCNT/PVP film, SWCNT/PVP/VHB without pre-strain, SWCNT/PVP/VHB with biaxial fabrication strain of 35%, SWCNT/PVP/VHB with uniaxial fabrication strain of 80%, and BSPF₁ and BSPF₇ with biaxial fabrication strain of 35%. For calculation of conductivity, the total thickness including VHB was considered.

so that no delamination occurred during the stretch-release-induced buckle formation (Fig. S7). In addition, the adhesion between two or multi- SWCNT/PVP layers is very strong due to the strong van der Waals forces between CNTs and PVP, as well as the entanglements between CNTs and PVP chains. Interestingly, the pore surface of PP foam also buckled along with the SWCNT/PVP layer (Fig. S22). These properties endow the conductive network with good structural integrity during microstructural changes of the BSPF_m.

Interestingly, we observed different morphologies for the biaxial buckled structures of the SWCNT conductive network (Fig. 5a–c). To understand the formation mechanism of these different types of morphologies, we performed finite element analysis (FEA) of the buckling of the SWCNT layer on the pores with bi-directional pre-strain. A 3D representative volume element (RVE) model was established for a single pore that contained SWCNT/

PVP film on the PP substrate. Analysis showed that the buckle morphology of the film-on-pore substrate was highly sensitive to the imperfections of SWCNT layer during the release of the biaxial pre-strain. Similar structures were predicted as experimentally observed by choosing different imperfections in the conductive layer (Fig. 5d–f).

We next investigated the microstructural evolution of BSPF_m during deformation. A biaxial BSPF₁ and a uniaxial BSPF₁ were uniaxially stretched to different strains (30% and 70%), and the cross-sectional images along the stretching direction were obtained on SEM (Fig. 5g–l and Fig. S23). Under stretching, the parallel buckles in the uniaxial BSPF₁ separated gradually, and interestingly the density of orthogonally interconnected buckles in both directions for the biaxial BSPF₁ decreased. Wrinkles perpendicular to the stretching direction were observed for biaxial and uniaxial BSPF₁, due to the Poisson's ratio

Figure 5 Microstructural analysis and FEA. (a–c) Different morphologies in SEM images for BSPF₁ with 35% biaxial pre-strain. (d–f) Morphologies observed in FEA modeling similar to the experimental results in (a–c) for biaxial buckles by choosing different imperfections in the conductive layer. (g–l) SEM images for cross-sections of 35% biaxial pre-strain BSPF₁ at applied strains of 0%, 30% and 70%.

effect (size decrease in the direction perpendicular to the stretching direction) (Fig. S24).

The formation and unfolding of the buckles help maintain the SWCNT conductive network intact during stretch and keep resistance stable. As a comparison, we stretched a SWCNT/PP foam composite that was prepared without using pre-strain, and obvious cracks were observed by stretching to 70% strain, with SWCNTs being stretched out (Fig. S25). Note that the conductive layer was made by inter-connecting of 1D SWCNT bundles in the 2D surface. The re-organization of the SWCNT bundles that packed in the conductive layer might also partially accommodate the applied strain [40,41]. Furthermore, the micro pores were highly deformed and flattened under stretch, as shown in Fig. 5g–i and Fig. S25a–c, which can help to share the applied strain under the foam. This is another advantage of using interconnecting pores as a skeleton to construct the conductive network. For comparison, we prepared a

SWCNT/PVP film on VHB tape, a buckled SWCNT/PVP on 35%-biaxially pre-strained VHB, and a buckled SWCNT/PVP on 80%-uniaxially pre-strained VHB, which showed dramatic increase (>1000%) in resistance when stretched to 5%, 60%, and 75% strains, respectively (Fig. 4b). Consequently, the flattening of pores, together with buckles unfolding, contributed importantly to the stable resistance of the interconnecting SWCNT network under large deformation.

Applications of BSPF_m

Stretchable EMI shielding

With the development of wearable electronic devices, protection of human and devices that are sensitive to the electromagnetic pollution is highly desired. The BSPF_m showed highly stable resistance under large stretch (e.g., 2.0% and 3.8% of $\Delta R/R_0$ for uni- and biaxial BSPF₁ at 70% of strain, respectively) and large content of micro pores

(90% porosity). This stretchable interconnecting conductive network would be a good candidate for EMI shielding under large deformation. Below we investigated the EMI SE at G-band (8–12 GHz) for BSPF_m of 35% biaxial fabrication strain, as a function of SWCNT content and applied strain. If not specified, the BSPF_m composites had a thickness of 2 mm. Fig. 6a shows that the average EMI SE increased from 11 to 45 dB with increasing the SWCNT contents from 3.8% ($m=1$) to 30.9% ($m=7$).

We then investigated the EMI SE of the BSPF_m at different applied strains. Fig. 6b shows that the average EMI SE only slightly decreased from 45 to 39 dB as the BSPF₇ (with SWCNT content of 30.9 wt%) was stretched from 0% to 30% strain. Detailed study about the reflection (SE_R) and absorption (SE_A) indicates that the electro-

magnetic wave was largely absorbed rather than reflected by the BSPF_m (Fig. S26a, b). This is possibly because stretching caused flattening of micro pores, and then decreased the multi-reflection inside the foam [42,43]. Repeatedly stretching and releasing BSPF₇ for 500 cycles up to 30% strain showed negligible decrease in EMI SE (Fig. 6c).

Tumor ablation

Thermal therapy of tumor is an important way for cancer treatment, in which the tumor tissues are subjected to a temperature higher than 45°C [44]. Photo-, magneto-, and electro-thermal tumor removal have been proved to be effective as an alternative to the direct tumor removal by surgery [45–47]. By considering that the BSPF_m showed a bulk conductivity and stable resistance during

Figure 6 Electromagnetic shielding properties of BSPF_m at 8–12 GHz and electro-thermal tumor removal using BSPF_m. (a) EMI SE as a function of frequency for BSPF_m having different SWCNT contents. (b) EMI SE as a function of frequency for BSPF₇ at different applied strains. (c) The EMI SE of the BSPF₇ after 500 cycles at 30% tensile strain. (d) Temperature as a function of time for BSPF₅ at different applied voltages. The insets were thermal images at 5, 10, 15, and 20 V. (e) Temperature as a function of time for BSPF₅ at different applied strains under 10 V voltage. The insets were thermal images at strains of 0%, 30%, and 50%. (f) Tumor volume and body weight as a function of time for the tumor-removal mice by thermal ablation and for the control mice. (g) Optical images before (i) and during (ii) thermal ablation of tumor tissue using BSPF₅ and thermal images of tumor tissue covered with (iii) and uncovered with (iv) BSPF₅ during thermal ablation. (h) Photographs showed the tumor tissue grown in the control mice in 20 days (left) and removed in treatment mice in 20 days (right).

large deformation, we here demonstrated the use of a biaxial BSPF₅ as an electrode for electro-thermal tumor removal. An advantage of using BSPF_m for heating is that the electricity can be applied on one side and the opposite side can also be heated due to the bulk conductivity. This would facilitate the operation during surgery. A biaxial BSPF₅ with a dimension of 1.0 cm × 1.1 cm × 0.15 mm was used in this study, and its electro-heating properties under different applied voltages and different applied strains were first investigated. The temperature of the BSPF₅ reached a plateau of 84.5°C within 18 s by applying a voltage of 12.5 V, and decreased in 13 s upon removal of the voltage (Fig. 6d). The plateau temperature increased from 37 to 140°C by increasing the voltage from 5 to 20 V, indicating that temperature can be easily controlled by using different voltages. Stretching the BSPF₅ from 0% to 50% strain with 10 V of voltage decreased the plateau temperature from 64 to 50°C (Fig. 6e), which is high enough for tumor removal. This high flexibility would enable good contact of the electrode with irregular tumor surface. Thermal images in the insets in Fig. 6d and e indicate uniform temperature distribution on the BSPF₅ surface, which is important for the operation in tumor removal.

We then investigated the *in vivo* electro-thermal tumor removal using BSPF₅ on Hepa1-6-tumor-bearing mice, with the tumor tissue embedded below the skin of abdomen (Fig. 6f–h). The experimental details refer to the Supplementary information. All animal procedures were performed according to the protocol approved by the Institutional Animal Care and Use Committee at China Pharmaceutical University (Permit Number: CCPU 2018-056). A BSPF₅ with size of 1.2 cm × 2.5 cm × 0.15 mm was connected with two copper wires on both ends using silver paste. The BSPF₅ was wrapped over the tumor (Fig. 6g(ii)), and a 12.5 V voltage was applied for heating for 30 min, corresponding to a power density of 0.26 W cm⁻². The temperature of the top surface of BSPF₅ increased to 84.5°C in 3 min and kept at this temperature for 30 min to heat the tumor tissue (Fig. 6g(iii)). And the tumor surface was at a temperature of 54.2°C during treatment (Fig. 6g(iv)). The electro-thermal treatment was repeated for another two times every five days. The mice were weighed every day after tumor ablation to monitor the health conditions, and the tumor size was also measured every day after treatment. It was shown that there was negligible change in body weight for all mice (Fig. 6f). For the tumor-removal mice, the tumor size decreased gradually and even entirely disappeared, and no recurrence of tumor was observed (Fig. 6f and h,

right). As a comparison, the control experiments showed that the tumor-bearing mice showed increased tumor size after 20 days of observation (Fig. 6f and h, left). The cell viability was tested on C2C12 cells by using (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) tetrazolium (MTT) assay, terminal deoxynucleotidyl transferase-mediated dUTP-digoxigenin nick-end labeling (TUNEL) assay, and cell attachment. The BSPF₅ showed low *in vitro* cell toxicity (Figs S27 and S28), indicating high biological safety when the BSPF_m were used for tumor therapy.

CONCLUSIONS

Buckled structures were introduced into the 3D conductive network of an intrinsic elastic conductor, enabling uniform bulk conductivity and stable resistance under large deformation. This was realized by self-assembly of SWCNT/PVP dispersion on the interconnecting pore surface of a pre-strained PP foam (to prepare the conductive network), and strain relaxing to enable buckle formation. The resulting buckled intrinsic conductor showed resistance variation as low as 2.0% for 70% strain and a quality factor as low as 0.028. Both unfolding of buckles and flattening of micropores contributed to the stability of the resistance under deformation. Microstructural analysis illustrated different patterns of 2D buckling structures, as simulated by FEA, which is due to the imperfections in the conductive layer. These properties enabled their applications as all-directional interconnects, EMI shielding, and tumor ablation electrodes. Our strategy could be applied to other polymer matrices (including PU, PDMS, and natural rubber) and other conductive fillers (including metal nanowires and nanoparticles, graphene, and MXene) to improve the electrical and mechanical properties, as well as incorporating other functionalities. This would expand their applications for wearable electronics and smart robotics.

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Conflict of interest The authors declare that they have no conflict of interest.

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具有褶皱导电路径的本征体弹性导体用于柔性电磁屏蔽和肿瘤消融

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摘要 弹性导体在可穿戴电子设备和软机器人中至关重要。理想的本征弹性体导体在大形变下显示出均匀的三维导电网络结构和稳定的电阻变化。其面临的一个挑战是, 由于体弹性导体在形变下导电路径断开, 电阻变化很大。我们的策略是将具有互连微孔的泡沫进行预拉伸, 通过碳纳米管在微孔表面自组装形成导电层, 随后释放预应变, 从而在导电网络中引入褶皱结构。在拉伸过程中, 褶皱和微孔的变形都有助于电阻的稳定(在70%应变下电阻变化2.0%)。微观结构和有限元分析表明, 由于导电层中的缺陷, 可以获得不同形貌的二维褶皱结构。我们展示了其在全方位电气互连、可拉伸电磁屏蔽和电热肿瘤消融方面的应用。