A Composite Elastic Conductor with High Dynamic Stability Based on 3D-Calabash Bunch Conductive Network Structure for Wearable Devices

Zhe Yu, Jie Shang,* Xuhong Niu, Yiwei Liu, Gang Liu, Pravarthana Dhanapal, Yanan Zheng, Huali Yang, Yuanzhao Wu, Youlin Zhou, Yuxin Wang, Daxiu Tang, and Run-Wei Li*®

As an indispensable basic component of wearable devices, the composite elastic conductor is widely used for elastic electrode and elastic wire. The ideal elastic conductor is expected to have high conductivity and stretchability, and maintain the resistance constant during stretching. However, it’s difficult for the current composite elastic conductors filling solid conductive materials. Here, a composite elastic conductor filling liquid-metal alloy is reported. Highly conductive and freely deformable liquid-metal filler achieves the elastic conductor with excellent conductivity and stretchability (electrical conductivity of $1.34 \times 10^3$ S cm$^{-1}$, sheet resistance of 17.59 mΩ $\square^{-1}$, and breaking elongation of 116.86%). Importantly, the filler forms novel three-dimensional Calabash Bunch conductive network structure in elastic matrix, which enables the elastic conductor to have excellent dynamic stability during stretching. The relative resistance variation is only 4.305% at 116.86% strain. This variation is 2–5 orders of magnitude smaller than that of the reported composite elastic conductor at the same strain, which is important for wearable devices to remain performances fairly unchanged undergo large deformation. Finally, it served as elastic electrodes of a stretchable capacitive strain sensor and elastic wires of a stretchable earphone respectively to demonstrate its potential in wearable devices.

1. Introduction

The wearable devices have high potentials for wide range of applications, such as artificial electronic skin,[1–8] mobile health care,[8–15] motion detection,[8,9,11,13,15–19] etc. Because the composite elastic conductor has low-cost, scalable, and simple production methods,[20–24] it is attracting intensive attention as indispensable basic component of wearable devices.[14,15,23–27] such as elastic electrode and elastic wire.[4,8,19–21,28–32] In this regard, researchers have developed several composite elastic conductors based on different types of conductive fillers,[25,26] including carbons,[8,31–34] metals,[21,35–37] conducting polymers,[27,38–40] and mixtures of two or more of them.[29,41–43] The ideal elastic conductor is expected that it not only has high conductivity and high stretchability simultaneously, but also its resistance is constant during deforming, in order to maintain the performances of wearable devices stable undergo large deformation.[21,36,44–46] However, it is still the primary cause of this is that there is a serious mismatch of elastic modulus between solid conductive fillers and polymer matrixes, a difference of 5–7 orders of magnitude.[12,23,25,26,46,47] The stretchability of composite elastic conductors will deteriorate with increasing the filling volume of solid conductive fillers, although the conductivity can be improved.[7,32] Moreover, the solid conductive fillers communicate with each other to form a conductive network. The gaps between the solid conductive fillers will be changed during stretching (Video S1, Supporting Information), which leads to significant resistance variation, i.e., the poor dynamic stability.[20,28,31–36] In general, the resistance values will increase 2–1000 times at 100% stretching strain.[9,20,29,35,38,48,49] And it is difficult to recover to the initial resistance values after unloading the strain, due to the sliding of stiff fillers in the elastic matrixes.[4,21,29,33]
To solve the above issues, the effective method is to choose a proper conductive filler to eliminate the mismatch of elastic modulus and design an appropriate mechanical structure to further improve the dynamic stability. The room-temperature liquid-metal (LM) with high conductivity is a perfect filler for elastic conductor. The excellent deformability makes it fully matching the mechanical behavior of polymer matrix and is capable of withstanding significantly large strain while maintaining electrically conductive (Video S1, Supporting Information). Therefore, tremendous efforts have been made in recent years to obtain the high conductive and stretchable LM-based composite elastic conductors utilizing different preparation methods. The common preparation method is directly injecting LM into elastic microchannel or patterning LM onto elastomer and then sealing. The injecting method is a relatively simple approach, but its practical application is limited because extremely high injection pressures (>1 MPa) and long injection times are required. The patterning method is relatively easy to design different mechanical structure for improving dynamic stability, but its preparation process is more tedious and less controllable. Hence, it is essential to design a suitable mechanical structure to improve dynamic stability of the LM-based composite elastic conductor by using a new and simple method.

In this paper, the liquid-metal alloy galinstan (GaInSn, 68.5%Ga, 21.5%In, and 10%Sn by mass, respectively) and polydimethylsiloxane (PDMS) were chosen to prepare the LM-based composite elastic conductor. Galinstan is a popular LM because of its lower melting point (theoretical temperature: −19 °C), high conductivity (≈3.4 × 10^4 S cm⁻¹), and nontoxicity. For PDMS, it is a common biomaterial with high stretchability. By combining galinstan and PDMS, a particular LM-based composite elastic conductor with double-layer structure is reported for the first time, including a galinstan/PDMS conducting layer and a pure PDMS supporting layer. In the conducting layer, galinstan is filled in the PDMS and forms a three-dimensional (3D) Calabash Bunch conductive network that ensures high dynamic stability during stretching. Moreover, adding a pure PDMS supporting layer is just for providing mechanical support and protecting the conducting layer from being damaged during stretching.

The results show that the LM-based composite elastic conductor with 3D-Calabash Bunch conductive network has an excellent electrical conductivity as high as 1.34 × 10^4 S cm⁻¹, low sheet resistance of 17.59 mΩ, and large breaking elongation of 116.86%. More importantly, it has excellent dynamic stability during stretching. The relative resistance variation (ΔR/R₀) is only 4.305% at 100% stretching strain, which exhibits a great promise as high-performance elastic electrodes and elastic wires. As elastic electrodes, a stretchable capacitive strain sensor was manufactured. It showed excellent linear response (R² = 0.999), high gauge factor (GF = 0.998), fast response time (<40 ms), low detection strain (<1%), and good stretching cyclic stability, which enable the sensor to be applied on intelligent data glove to detect the motion of finger and gesture of hand well. As elastic earphone wires, a stretchable earphone was manufactured. It also showed fine music signals transmission ability similar to that of common copper-wire earphone, even after stretching to twice its original length.

2. Results and Discussion

Recently, the LM-based composite elastic conductors with high conductivity and stretchability become hot topic. The reported LM-based composite elastic conductors can be excellent as elastic wires, but they are unapplicable to be served as elastic electrodes. And more importantly, their dynamic stability is still not ideal for practical application. To improve the dynamic stability, some special mechanical structures have been reported in the solid-filler-based composite elastic conductors, such as wrinkled structure, bisheath structure, and fractal structure. All these mechanical structures release strain through wrinkles of conductors, so that the surface morphology will have a great change during stretching, which makes it difficult to serve as electrode. Here, a Calabash Bunch structure, which is consisted of multiple balls connected one by one, is put forward to improve the dynamic stability. As a model, we injected galinstan into the rubber tube with Calabash Bunch structure, and stretched it out to 50% and 100% strain, respectively. The stretching process is displayed in Figure 1a. From the picture we can see that the stretching strain is mainly released by the calabash balls with bigger curvature, and there is only a slight deformation at the necked connections between the balls. The thin necked connections are indeed the major contributor of overall resistance. Therefore, using this Calabash Bunch structure, it is possible that the resistance variation is suppressed to a lower level during stretching. In order to verify our thoughts, its resistance variation was measured during stretching, and it was compared with that of galinstan-filled rubber tube with cylindrical structure. The results are shown in Figure 1b. As can be seen from the picture, the relative resistance variation of galinstan-filled rubber tube with cylindrical structure reaches up to 265.56% at 100% stretching strain, which is similar as the reported LM-based composite elastic conductors. Whereas the relative resistance variation of galinstan-filled rubber tube with Calabash Bunch structure is only 4.83% under the same stretching strain. This resistance variation is negligible compared with that of galinstan-filled rubber tube with cylindrical structure. Moreover, Liang et al. and Park et al. found that 3D LM network could also improve the dynamic stability of composite elastic conductors. However, this 3D-LM conductive network is fragile and easy to be damaged under repeated stress. Obviously, if the conducting layer has a galinstan-filled 3D-Calabash Bunch conductive network structure and a supporting layer to protect the fragile conducting layer, there will be a greater chance to get a composite elastic conductor with excellent conductivity, stretchability, and dynamic stability.

It is a preferred strategy to obtain desired LM-based composite elastic conductor by 3D self-shaping strategy of multicomponent combination. For this, we fully took advantage of the significant features of galinstan, including high density, large surface tension, and oxidation property. The fabrication process of hierarchical LM-based composite elastic conductor, including elastic electrode and elastic wire, is schematically illustrated in Figure S1 of the Supporting Information. It is worth mentioning that the LM-based composite elastic wire is prepared by electronic printing, and the specific process is inspired by the work of Jiang et al. During stirring, the large surface tension
makes galinstan microdroplets be globular as the balls of Calabash Bunches, and the oxidation property makes galinstan microdroplets be coated by a thin passivating oxide skin (≈1 nm thick), which can stabilize the shape of microdroplets and has almost no influence on the conductive.⁹⁰,⁹¹ During standing, the high density makes the mixture to be hierarchical, and the microdroplets connect with others to be a 3D-Calabash Bunch structure. The exploration of important preparation parameters is shown in Figure S2 of the Supporting Information. Figure 1c gives the scanning electron microscope (SEM) cross-sectional view of the prepared sample. It is evident from the picture that the prepared LM-based composite elastic conductor has the expected structure, which is consisted of a pure PDMS supporting layer and a galinstan/PDMS conducting layer, and their thickness can be controlled. Notably, the galinstan/PDMS conducting layer formed into our desired 3D-Calabash Bunch conductive network structure. The more SEM pictures of 3D-Calabash Bunch conductive network structure can be seen in Figure S3 of the Supporting Information. Figure 1d,e shows the optical images of the prepared elastic electrode and elastic wire at the initial state and the stretched state, which display excellent stretchability.

Next, the conductivity and stretchability of the prepared LM-based composite elastic conductor were tested. Figure 2a shows the mapping image of sheet resistances for the sample with length of 100 mm and width of 40 mm, which is measured by four probe measurements. The data reveal that the sheet resistances are between 11.05 and 28.83 mΩ□⁻¹, with a mean of 17.59 mΩ□⁻¹, as shown in Figure 2b. Moreover, the bulk conductivity, stretchability, and dynamic stability were also tested using the international standard (ISO37: 2005) samples, as shown in the inset of Figure 2c. As can be seen from Figure 2c, the bulk conductivity is as high as $1.34 \times 10^3$ S cm⁻¹ and a good stretchability is demonstrated. The breaking elongation and breaking strength by uniaxial stretching are $\approx116.86\%$ and $\approx0.732$ MPa, respectively. According to the Young’s modulus formula

$$E = \sigma /\varepsilon$$

where $E$ is Young’s modulus, $\sigma$ is stretching stress, and $\varepsilon$ is stretching strain. The Young’s modulus of the prepared LM-based composite elastic conductor is derived to

Figure 1. a) Optical images of the galinstan-filled elastic rubber with Calabash Bunch structure under the strain of 0%, 50%, and 100%, respectively. b) Relative resistance variations ($\Delta R / R_0$) as a function of stretching strain for the galinstan-filled rubber tubes with Calabash Bunch structure and cylindrical structure. Inset shows the schematic illustrations of Calabash Bunch structure and cylindrical structure. c) Scanning electron microscope (SEM) cross-sectional view of the prepared LM-based composite elastic conductor with the desired 3D-Calabash Bunch conductive network structure in PDMS matrix. d) Optical images of the prepared LM-based composite elastic electrode at initial and stretched states. e) Optical images of the prepared LM-based composite elastic wires at initial and stretched states.
be ≈ 0.655 MPa. In order to show the influence of galinstan on the mechanical property of PDMS matrix, the stress-strain curve of pure PDMS prepared by ourselves was also measured, as shown in Figure S4 of the Supporting Information. The breaking elongation and breaking strength of our pure PDMS by uniaxial stretching are ≈ 128.62% and ≈ 0.782 MPa, respectively, and the calculated results show that its Young’s modulus is ≈ 0.608 MPa by Equation (1), which is consistent with the reported. It is easy to see the prepared LM-based composite elastic conductor and pure PDMS have the similar stretchability. The slight discrepancy may be attributed to the surface tension of the liquid-solid interface, and this phenomenon is quite common in other liquid-filled composite materials. In the same time, it can also be seen from Figure 2c, the relative resistance variation caused by strain is only ≈ 4.305% at the maximum stretching strain of 100%, which is 2–5 orders of magnitude smaller than that of the reported composite elastic conductor at the same strain. This fully demonstrated the prepared LM-based composite elastic conductor has high dynamic stability. The testing process can be observed in Video S2 of the Supporting Information.

Figure 2. a) The mapping images of sheet resistances for the prepared LM-based composite elastic conductor with 3D-Calabash Bunch conductive network structure. b) The corresponding statistical histograms calculated from (a). c) Typical resistance-strain and stress-strain curves. Optical image of stretching sample is shown in the inset. Scale bar in the inset is 2 cm. d) Relative resistance variation (ΔR/R₀) as a function of stretching strain during load–unload operation with different maximum stretching strains. Inset shows the hysteresis coefficient of the load–unload curves. e) Typical 3000 cycle test. The maximum stretching strain is 80%. f) Relative resistance variation (ΔR/R₀) as a function of stretching strain during load–unload operation at different temperatures.
Further, the dynamic stability was evaluated under different stretching conditions, including stretching velocity, load–unload operation, and stretching time. For the effect of stretching velocity on the dynamic stability, Hu et al. found the resistance of composite elastic conductor based on copper nanowires and polyurethane increased by 850% and 2560% at 60% strain with the stretching velocity of 0.6 and 60 mm min⁻¹, respectively.[8] Chung et al. found the resistance of wave structured silver elastic conductor increased by 45% and 174% at 20% strain with the stretching velocity of 1 and 64 mm min⁻¹, respectively.[85]

However, the resistance of the prepared LM-based composite elastic conductor only increased by 0.236% and 3.415% at 50% strain with the stretching velocity of 0.35 and 175 mm min⁻¹, respectively (Figure S5, Supporting Information), which is 2–4 orders of magnitude smaller than that of the above two common solid-filler-based composite elastic conductors.

Moreover, the solid-filler-based composite elastic conductors often have a large hysteresis coefficient (0.15–0.55) and poor fatigue resistance (increasing about 1–3 orders of magnitude at 100% strain) because of the slide of solid fillers.[9,15,35,36] For the prepared LM-based composite elastic conductor, the superior deformation capability of galinstan and novel 3D-Calabash Bunch conductive network structure also offer the benefit of decreasing hysteresis coefficient and improving fatigue resistance. Figure 2d shows the load–unload operation. It can be found that although the hysteresis coefficients go up with the increase of strain, as shown in the inset of Figure 2d. But it is only 0.064 at 100% strain. Moreover, the resistance of the prepared LM-based composite elastic conductor only changes 3.301% after 3000 stretching cycles when the maximum stretching strain is 80%, as shown in Figure 2e. In short, the prepared LM-based composite elastic conductor has excellent dynamic stability, which is less affected by the stretching velocity, load–unload operation and stretching time.

Comparing with the reported elastic conductors (shown in the Table 1), especially of those based on solid fillers, the prepared LM-based composite elastic conductor shows high conductivity, good stretchability, and excellent dynamic stability. Nevertheless, the above comparisons are all in two completely different samples. Therefore, it is necessary to compare the performances within the same sample. Hence, the influence of the galinstan fillers before and after curing on the dynamic stability was explored within the operating temperature range of PDMS matrix (from −40 °C to 150 °C).[27,82] The melting temperature and crystallization temperature of galinstan prepared by ourselves were measured by differential scanning calorimetry. As can be seen from Figure S6 of the Supporting Information, the melting temperature (T_m) and the crystallization temperature (T_c) are ≈9.44 °C and ≈−0.16 °C, respectively. The resistance variations of the same sample were measured during load–unload operation in different ambient temperatures, as shown in Figure 2f. From the figure, it can be seen that ΔR/R_0 are only ≈3.97% and ≈4.20% at 60% stretching strain when the measure temperatures are 25 °C (above the crystallization temperature) and 0 °C (near the crystallization temperature), respectively. But at −25 °C (under the crystallization temperature), it reaches about 6000% when stretching strain is only ≈20%. In addition, there is a large electrical hysteresis like the solid-filler-based composite elastic conductor.[21,35,36] This fully showed the advantages of the prepared LM-based composite elastic conductor.

Besides the common stretching strain, the impact of other kinds of strains was also researched, including bending strain, twisting strain, pressing strain, and complex strain. Figure 3 shows the dynamic stability of the prepared LM-based composite elastic conductor under bending, twisting, and pressing strains. The tests of all three types of strains are represented high conductivity, good stretchability, and excellent dynamic stability. Nevertheless, the above comparisons are all in two completely different samples. Therefore, it is necessary to compare the performances within the same sample. Hence, the influence of the

Table 1. Comparison of our LM-based composite elastic conductor with reported composite elastic conductors.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Conductive area [S cm⁻¹]</th>
<th>R_0 [Ω cm⁻¹]</th>
<th>ΔR/R_0 @ stretching strain</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag nanowire/PDMS</td>
<td>0.024</td>
<td>359.77% @ 80%</td>
<td></td>
<td>[21]</td>
</tr>
<tr>
<td>Graphene-Ag nanowire/PDMS</td>
<td>0.024</td>
<td>250% @ 40%</td>
<td></td>
<td>[41]</td>
</tr>
<tr>
<td>Au clusters/PDMS</td>
<td>≈500</td>
<td>1726.09% @ 40%</td>
<td></td>
<td>[35]</td>
</tr>
<tr>
<td>Graphene/PDMS</td>
<td>≈280</td>
<td>900% @ 25%</td>
<td></td>
<td>[31]</td>
</tr>
<tr>
<td>10 vol% Polyaniline/poly(styrene-co-ethyl-cenebutylene-co-styrene)</td>
<td>≈450</td>
<td>–10 225% @ 100%</td>
<td></td>
<td>[38]</td>
</tr>
<tr>
<td>Single-walled carbon nanotube/Polyurethane</td>
<td>–242</td>
<td>341.04%@100%</td>
<td></td>
<td>[49]</td>
</tr>
<tr>
<td>Galinstan/PDMS</td>
<td>0.024</td>
<td>4.31% @ 116.86%</td>
<td></td>
<td>Our work</td>
</tr>
</tbody>
</table>
are summarized in Table 2. It can be found the relative resistance variations of the prepared LM-based composite elastic conductor are all within 6.19%.

Table 2. The relative resistance variations of the prepared LM-based composite elastic conductor with 3D-Calabash Bunch conductive network structure under bending, twisting, and pressing strains.

<table>
<thead>
<tr>
<th>Type of Strain</th>
<th>Maximum resistance variation@maximum deformation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Load-unload</td>
</tr>
<tr>
<td>Bending</td>
<td>6.19%@folded</td>
</tr>
<tr>
<td>Twisting</td>
<td>3.52%@720°</td>
</tr>
<tr>
<td>Pressing</td>
<td>4.33%@500 kPa</td>
</tr>
</tbody>
</table>

Figure 3. Load–unload curves and relative resistance variations ($\Delta R/R_0$) as a function of strain for 1000 cycles, including a,b) bending strain, c,d) twisting strain, and e,f) pressing strain. The dimension of the samples are 30 mm long, 20 mm wide, and 2 mm high. Insets of (a), (c), and (e) show the schematic illustrations of bending test, twisting test, and pressing test, respectively.

Figure 4 shows the dynamic stability of the conductivity under the complex strain. It consists of two stages: First twist 360° and then stretch the twisted sample until it breaks, as shown in Figure 4a,b. In the first stage, the resistance of the prepared LM-based composite elastic conductor gradually increases with the increase of twisting angle, but the maximum relative resistance variation is only $\approx2.15\%$. In the second stage, the resistance of the prepared LM-based composite elastic conductor first decreases and then increases with the increase of stretching strain, and reaches the maximum variation at the limit strain by uniaxial stretching of $\approx78.79\%$. The maximum relative resistance variation is also only $\approx4.20\%$. Figure 4c shows the cycle performance, and each cycle consists of two stages: First twist 360° and then stretch the twisted sample to
≈1.7 times its length. As can be seen from the picture, the resistance of sample decreases only ≈2.99% after 200 cycles. Clearly, the dynamic stability of the prepared LM-based composite elastic conductor is still excellent under the bending, twisting, pressing, and complex strains, which is critical for the applications. For purposes of demonstration, a stretchable capacitive strain sensor and a stretchable earphone were manufactured, which adopted the prepared LM-based composite elastic conductors as elastic electrodes and elastic wires, respectively.

Wearable sensor technology is an emerging area and can be utilized for human motion monitoring, physiology monitoring, and human–machine interaction. The stretchable capacitive strain sensor with high linear response and low response hysteresis is a focal point of research. The typical stretchable capacitive strain sensor consists of stretchable upper and down electrodes and dielectric. The composite elastic conductors and silicone are the most commonly used electrode and dielectric materials, respectively. Each strain sensor has a different sensitivity to strain, which is expressed quantitatively as the GF. The gauge factor of the capacitive strain sensor is defined with the following equation:

\[
GF = \frac{\Delta C}{C_0 \epsilon} = \left[ \frac{1}{1 - \nu_{\text{Dielectric}}} - 1 \right] \epsilon
\]

where \(C_0\) is the initial capacitance, \(\Delta C\) is the capacitance variation, \(\epsilon\) is the uniaxially stretching strain, and \(\nu_{\text{Electrode}}\) and \(\nu_{\text{Dielectric}}\) are the Poisson ratios of the electrode and dielectric, respectively. When \(\nu_{\text{Electrode}}\) equals \(\nu_{\text{Dielectric}}\), the GF will have an ideal value of 1. However, the Poisson ratios of the solid–filler-based composite elastic electrode and silicone dielectric are usually different and there are often big differences between them. Therefore, the gauge factors of the reported stretchable capacitive strain sensors are mostly less than 0.7. For instance, the sensors of Carbon nanotube/Ecoflex/Carbon nanotube and Ag nanowires/Ecoflex/Ag nanowires have a gauge factor of 0.4 and 0.7 within the sensing range of 50%, respectively. Here, a stretchable capacitive strain sensor with the prepared LM-based composite elastic conductor (galinstan/PDMS) as upper and down electrodes and PDMS as dielectric is reported, as shown in Figure 5a. The sensor is connected to the Inductance–Capacitance–Resistance Impedance Analyzer by Ag wires (inset of Figure 5a) in order to record capacitive variation during stretching. From this figure, you can see that the thickness of upper electrode, dielectric, and lower electrode are 400, 200, and 400 µm, respectively. Figure 5b shows the relative capacitance change \(\Delta C/C_0\) versus stretching strain to 50%. The strain sensor exhibits good linear response. The gauge factor is found to be 0.998, which is the slope of the linear fitting. The results indicated that the gauge factor is close to the theoretical value of 1. The excellent gauge factor chiefly thanks to the similar Poisson ratios of the prepared galinstan/PDMS electrodes and PDMS dielectric. Furthermore, it shows that our stretchable capacitive strain sensor also has good stretching cyclic stability from Figure S9 of the Supporting Information. During 1000 stretching cycles with the stretching velocity of
200 mm min⁻¹, the maximum capacitance response deviations at 0% strain and 50% strain are 1.43% and 1.11%, respectively. In addition, Figure 5c shows that the sensor can reliably detect the strain below 1%, and has a small time delay (Δt) relative to the actual strain loading. The four time delays (Δt₁, Δt₂, Δt₃, and Δt₄) are 36.5, 15.5, 42.5, and 31.5 ms, respectively. That means the sensor has a fast response time (20–40 ms). In short, our sensor has a good detecting sensitivity, cyclic stability, detecting precision, and response speed.

Compared with the resistive strain sensor, the capacitive strain sensor are ideal for applications where the strain is relatively large. Here, we assembled our sensor on the index finger joint to detect the bending movements of the finger. When the demonstrator’s finger was gradually bent, the capacitance of the sensor increased step by step (Action One to Six, Figure 6a), distinguishing every single slight bending. Then the capacitance also be able to returned to the initial value step by step when the finger was gradually unfolded (Action Six to Eleven, Figure 6a). Besides, the sensor could track the rapid movement of finger, and the sensor’s capacitance could remain constant when the finger was bent to the same angle (Figure S10 and Video S3, Supporting Information), thanks to the excellent stability and reliability of our sensor. The use of our sensor might benefit healthcare, including continuous health monitoring, daily and sports activity tracking, and so on. Moreover, we demonstrated a prototypical data glove by integrating our sensor onto a rubber glove to detect gestures according to the motion of each finger (Figure 6b). Experiments confirmed that our data glove would not have bound feeling. When different gestures were made (Figure 6c), five sensors on the data glove would have different capacitive responses respectively, thus enabling realize the precise detection of gestures (Figure 6d).

Earphone has been widely used with stationary CD and DVD players, home theater, personal computers, or portable devices (e.g., digital audio player/MP3 player, mobile phone). It has become part of modern life. However, the lengthiness and fracture of earphone wires have always annoyed users. Here, a stretchable earphone with the prepared LM-based composite elastic conductor (galinstan/PDMS) as earphone wires is reported. The width of earphone wire is less than 0.85 mm (Figure S11, Supporting Information) and its length is 100 mm, which exhibits the good stretchability, as shown in Figure 7a. In order to prove the electrical performance, its music signals (China’s national anthem) transmission ability was compared with common copper earphone wire. During performance testing, the oscilloscope was connected with the loudspeaker of earphone in parallel to record the music signals. As can be seen from Figure 7b, the stretchable earphone showed fine music signals transmission ability similar to that of common copper-wire earphone, even after stretching to twice its original length (100% strain). Figure 7c shows the amplitude deviations. The maximum amplitude deviations of music signals are only −0.051 and −0.075 V at 50% and 100% strain, respectively, which are almost negligible.
influence of applied stretching strains on the frequency characteristics of music signals was also analyzed, as shown in Figure S12 of the Supporting Information. The frequency spectrograms were obtained by Fourier transformation the voltage waveforms between 17 and 35 s of Figure 7b. It can be seen the frequency characteristics are similar regardless of stretching strain. In addition, the amplitude–frequency characteristics at the different stretching strain states were also tested through the oscilloscope from 1 Hz to 5 MHz (Figure S13, Supporting Information) to analyze the working frequency bandwidth. The results show that the maximum amplitude has a slight increase with the increase of the stretching strain. Even if the earphone wires are stretched to 100% strain, the maximum amplitude increases only 10.89% relative to the unstrain state. This is due to the resistances of our earphone wires almost constant at the different stretching strain states. Meanwhile, it can be seen from the amplitude–frequency curves that the stretching strain has no influence on the working frequency

Figure 6. a) A prototypical data glove. Upper: Optical pictures while the finger was gradually folded (Action One-Action Six) and then unfolded (Action Six-Action Eleven). Lower: Corresponding capacitive responses of stretchable capacitive strain sensor adopting the prepared LM-based composite elastic electrodes. b) Optical image of a prototypical data glove by integrating our sensor onto a rubber glove. c) Optical images of eight different gestures wearing data glove. d) Posture recognition of eight different gestures of (c).
bandwidth from 1 Hz to 100 kHz, which can fully meet the service requirements because hearing frequency range of human ear is about from 20 Hz to 2 kHz. In short, our stretchable earphone has a wide working frequency bandwidth and fine music signals transmission ability similar to that of common copper-wire earphone, even after stretching to twice its original length.

3. Conclusion

In this work, an elastic conductor with novel 3D-Calabash Bunch conductive network structure was successfully prepared using highly conductive liquid-metal alloy galinstan and highly stretchable PDMS. The prepared LM-based composite elastic conductor displays excellent performances. Its electrical conductivity, mean sheet resistance and breaking elongation are $1.34 \times 10^3$ S cm$^{-1}$, 17.59 mΩ $\square^{-1}$ and 116.86%, respectively. And more importantly, it is insensitive to strain. The relative resistance variation is only 4.305% while stretching to 100% strain, which is 2–5 orders of magnitude smaller than that of the reported composite elastic conductor. The dynamic stability is mainly ascribed to the deformable galinstan and novel 3D-Calabash Bunch conductive network structure. Moreover, it is less affected by the strain type, stretching velocity, load–unload operation, and
cyclic number. Combining good conductivity, stretchability, and dynamic stability, the prepared LM-based composite elastic conductor has a wide application prospect in the wearable devices, and its potential is demonstrated through integration into a stretchable capacitive strain sensor served as elastic electrodes and a stretchable earphone served as elastic wires, respectively.

4. Experimental Section

Preparation of Liquid-Metal Galinstan and LM-Based Composite Elastic Conductor with 3D-Calabash Bunch Conductive Network Structure: High purity metal gallium (99.99%; Beijing Founde Star Sci. & Technol. Co., Ltd), indium (99.995%; Beijing Founde Star Sci. & Technol. Co., Ltd), and tin (99.99%; Beijing Founde Star Sci. & Technol. Co., Ltd) were mixed together in the ratio of 68.2:21.8:10 by mass. Then the mixture was heated and stirred at 60 °C for 30 min in the water bath to obtain liquid-metal galinstan (Ga_{68.2}In_{21.8}Sn_{10}). The prepared galinstan and PDMS (Sylgard 184, Dow Corning Corporation) were mixed in the ratio of 1:3 by volume, which means galinstan is 25 vol% of mixture, and stirred together for 5 min and then make it stand at room temperature for 60 min. Next, the mixture was heat cured at 60 °C for 4 h to obtain the LM-based composite elastic conductor with 3D-Calabash Bunch conductive network structure. The detailed characteristics of preparation are shown in the Supporting Information.

Characterization of the Microstructure: The cross-sectional microstructures of LM-based composite elastic conductor, stretchable capacitive strain sensor, and LM-based composite elastic wire were characterized by the field-emission scanning electron microscopy (Sirion 200, FEI).

Measurements of Electrical Properties at Different Strain and Temperature: The resistance was measured using the DC current source (Keithley 6221) and the nanovoltmeter (Agilent 34420A) by the four-wire method. The measured temperature was controlled by an universal high-low temperature test chamber (JY-CD-120, Dongguan Jingyu Environment Test Equipment Co. Ltd.). Let the samples keep 16 h at each measured temperature to ensure that they could reach the setting temperatures and remove the interference of galinstan supercooling in low temperatures. The stretching strain and pressuring strain were applied by a universal material testing machine (Instron 5943). The bending strain and twisting strain were applied by the homemade bending and twisting equipment, respectively.

Preparation and Measurement of Stretchable Capacitive Strain Sensor: First, two LM-based composite elastic electrodes were prepared (Figure S1, Supporting Information) as upper and down electrodes of the stretchable capacitive strain sensor. Second, silver wires were connected to the different end of the two electrodes. Third, PDMS was spun on the bottom electrode as the dielectric layer. At last, the top electrode was placed on the uncured PDMS dielectric layer and cured at 60 °C for 4 h to obtain the stretchable capacitive strain sensor. The stretching strain was loaded onto the capacitive strain sensor by universal material testing machine (Instron 5943). At the same time, the capacitance variation was measured by an Inductance-Capacitance-Resistance Meter (IM 3570, HIOKI Impedance Analyzer).

Preparation and Measurement of Stretchable Earphone: The LM-based composite elastic wires were prepared using printing method. The detailed preparation crafts are shown in Figure S1 of Supporting Information. The samples were used as earphone wires to connect with the loudspeaker and jack to obtain stretchable earphone. For testing the voltage waveforms, the oscilloscope (710 110/DLM2024, Yokogawa) was connected with the loudspeaker in parallel to record the music signals. Similarly, the oscilloscope was connected with the elastic wire in parallel to test the amplitude-frequency characteristics. Moreover, stretchable earphone was stretched by the homemade stretching device with controlled motor.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Z.Y., J.S., and X.H.N. contributed equally to this work. This research was supported in part by the National Natural Foundation of China (61774161, 61704177, 51525103, and 11474295), China International Cooperation Project (2016YFE0126700), National Key Technologies R&D Program of China (2016YFA0201102), CAS President’s International Fellowship Initiative (PIFI), Public Welfare Technical Applied Research Project of Zhejiang Province (2017C31100), Ningbo Science and Technology Innovation Team (2015B11001), and the Natural Science Foundation of Ningbo (2017A610093 and 2017A610097).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

3D-Calabash Bunch conductive network structures, dynamic stability, elastic conductors, liquid metals, wearable devices

Received: March 5, 2018
Revised: May 28, 2018
Published online:


