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Highly Stable and Stretchable Conductive Films through Thermal Radiation-assisted Metal Encapsulation

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Abstract

Stretchable conductors are the basic units of advanced flexible electronic devices, such as skin-like sensors, stretchable batteries, soft actuators and so forth. Current fabrication strategies are mainly focused on the stretchability of the conductor with less emphasis on the huge mismatch of the conductive material and polymeric substrate which results in stability issues during long-term usage. Here we report a new approach of thermal radiation-assisted metal encapsulation (TRAP) to construct an interlocking layer between polydimethylsiloxane (PDMS) and gold by employing semi-polymerized PDMS substrate to encapsulate the gold clusters/atoms during thermal deposition. The stability of the stretchable conductor is significantly enhanced based on the interlocking effect of metal and polymer, with high

interfacial adhesion (> 2 MPa) and cyclic stability ($> 10,000$ cycles). Also, the conductor possesses superior properties as high stretchability ($> 130\%$) and large active surface area ($> 5:1$ effective surface area/geometrical area). It is noted that our method can be easily used to fabricate such stretchable conductor in a wafer scale format in a one-step process. As a proof of concept, both long-term implantation in an animal model to monitor intramuscular electric signals and on human skin for detection of bio-signals are demonstrated. This design approach brings about a new perspective on the exploration of stretchable conductors for biomedical applications.

Stretchable conductors are the basic building blocks of advanced flexible electronic devices, such as flexible display, skin-like sensors, stretchable batteries, soft actuators and so forth.^[1-10] They are used in a vast number of soft and stretchable devices developed in recent years, including bio-interfacing electrodes,^[11-15] transistors,^[16-18] mechanical sensors,^[19-22] energy devices^[23-26] and many more.^[27-42] To meet most application requirements, stretchable conductors need to remain conductive under tensile strain of more than 100%, and even more importantly, to show stable performance in terms of interfacial adhesion between conductive metal film and the supporting polymer substrate.^[1] Current methods to achieve stretchable conductors generally fall into two categories.^[43-67] One involves a structural design strategy, where the conducting material is designed with specific structures/topographies including serpentine,^[46-52] wrinkles,^[53,54] meshes,^[55-58] and micro-cracks.^[59-63] The other strategy relies on intrinsic stretchability of the conductive material including stretchable conducting polymers^[64] and liquid metal.^[65-67] These two strategies mostly focus on the achievement of stretchability, however, with less concern about the huge mechanical mismatch between conductive material (e.g., metal with modulus of GPa magnitude) and polymeric substrate (e.g., polydimethylsiloxane (PDMS) of MPa magnitude) which results in stability issues, e.g.,

poor interfacial adhesion, during long-term usage. Previously, we presented a method to construct nanopiles under the conductive film as the transitional layer to achieve stretchable conductors with high adhesion.^[63] However, this fabrication process is limited to small scale applications ($\sim \text{cm}^2$), and the stretchability achieved is rather small ($\sim 45\%$). Therefore, it remains a challenge to develop a readily accessible method to achieve high interfacial adhesion, high stability and high stretchability in a wafer scale format.

Firstly, in order to enhance the adhesion, the proposed design includes an interlocking layer to increase the interaction area between metal film and polymeric substrate (**Figure 1a,b**).^[68] The interlocking layer also influences the mechanical properties by regulating the strain distribution in the film (Figure 1a, bottom and Figure 1c) resulting in the formation of randomly distributed micro/nano-fractures in the conductive layer when the film is stretched. For flat films, the strain distributes uniformly across the entire film when a certain tensile strain is applied (Figure 1a, bottom and Figure 1c). This leads to macro crack formation through-out the conductive layer, which severely imparts its conductivity. Thus, we need to find a strategy to construct an interlocking layer with excellent adhesion, stretchability and conductive properties during operation.

During traditional thermal film deposition, the supporting substrate is employed to receive the metal atoms evaporated from the metal source, and the metal atoms typically stack on the solid substrate, but they cannot penetrate deeply into the supporting substrate. It is just like stacking metal balls on the rigid ground, which can be named layer-by-layer or 2D growth. However, if we employ a soft substrate, metal atoms can penetrate into the substrate, via 3D-diffusion, to form an interlocking layer. Therefore, we hypothesized that the semi-polymerized PDMS with certain fluidity can be used as the supporting substrate. The evaporated metal atoms/clusters could penetrate into the semi-polymerized PDMS during its gradual polymerization assisted by thermal radiation heat from the evaporation source

resulting in encapsulation of metal atoms/clusters by PDMS to form a composite interlocking layer (Figure 1d).

Herein, we report a new approach of thermal radiation-assisted metal encapsulation (TRAP) to fabricate highly stretchable and stable stretchable conductive metal films. It focuses on interfacial design of the conducting material and the polymeric substrate to fabricate high-performance stretchable conductors with high stretchability and stability, large surface area, and most importantly, high interfacial adhesion between gold and the elastic substrate, PDMS. A high stretchability ($> 130\%$) is achieved by strain redistribution via the unique interfacial layer between the gold layer and the PDMS substrate. High adhesion (> 2 MPa) is achieved because of the penetration of gold atoms into the polymer. Making use of these superior properties, we successfully demonstrate both long-term implantation in rats to monitor intramuscular electric signals and on-skin detection of human bio-signals for recovery monitoring of targeted muscle reinnervation. We also show that the novel stretchable electrodes can be implanted and entwined around the sciatic nerves in rats as neural stimulators, and the induced myoelectricity signal is successfully recorded. Our strategy will undoubtedly promote the development of high-performance stretchable conductors for practical application. Moreover, the TRAP film fabrication process is compatible with large scale production ($> 15\text{ cm} \times 15\text{ cm}$).

In a typical experiment, a semi-polymerized PDMS film prepared by controlling the pre-curing time is mounted in the evaporation chamber to receive gold atoms from a resistively heated crucible (Figure S1). Multiple physical and chemical processes occur at the interface between PDMS and gold. Initially, when gold atoms first strike onto the soft semi-polymerized PDMS, metal diffusion occurs due to fluidic character of the semi-polymerized PDMS (Figure 1d). Moreover, heat transfer from the source facilitates PDMS polymerization (Figure S1a, b). When PDMS film is fully cured, no more diffusion occurs at the interface, and the gold layer grows in thickness (Figure 1d) resulting in a composite interlocking layer

between the metal film and PDMS. During the entire process, heat transfer at the interface is critical for obtaining a desirable interlocking structure. Therefore, we estimated the temperature field in the semi-cured PDMS substrate by establishing the heat transfer equation of the film (see details in Supporting Note 1 and 2). Here, all terms are expressed in per unit area. We consider the following heat contributions: heat input from the thermal radiation, Q_I , heat dissipation due to thermal radiation at both sides of the film, Q_{d1} and Q_{d2} , and thermal conduction at the backing, Q_{d3} (heat convection is omitted in high vacuum). Under the hypothesis of quasi-steady heat-transfer state and the negligible heat consumption of PDMS polymerization, we have (Figure S1c,d and Supporting Note 1):

$$Q_I = Q_{d1} + Q_{d2} + Q_{d3} \quad (1)$$

Considering the model of thermal resistance (Figure S1c, d), we further obtain (Supporting Note 2):

$$T_{\text{PDMS}} = T_0 + A Q_I \times (R_P + R_g + R_{r2}) \quad (2)$$

where T_0 is the environmental initial temperature (23 °C), A is the surface area of PDMS film, R_P , R_g , R_{r2} is the thermal resistance of heat conduction in PDMS, in backing glass and heat radiation from glass to the whole chamber, respectively. Finally, the temperature of a PDMS film under thermal radiation is calculated as ~ 93 °C (see details in Supporting Note 2), at which it could be fully cured in around half an hour. Since the thermal evaporation rate is slow (usually ~ 0.5 Å/s), and given that it takes around 100 minutes to deposit a 300 nm thick film, the entire substrate is fully polymerized during this process.

The TRAP film can be fabricated in a large scale of hundreds of centimeter square (**Figure 2a**), and it appears in dark color at the reverse side of the film (Figure 2b) because of the 3D diffusion effect of gold atoms in PDMS. From the cross-sectional field emission scanning electron microscope (FESEM) image, we can clearly observe the interfacial structure (Figure 2c,d and Figure S2a,b). Basically, the film consists of three layers: 1) a gold conducting layer at the top; 2) a composite layer with interlocking of PDMS and gold in

between (inset of Figure 2d); 3) PDMS substrate at the bottom (Figure 2d). Besides, the film surface adopts a randomly wrinkled morphology (Figure 2e,f) induced by the modulus mismatch between gold and PDMS during the dynamic polymerization process. The appearance of wrinkles is dependent on the ratio of PDMS monomer to cross linker and pre-curing time (Figure S3). When investigated in detail, the wrinkled film is composed of gold nanoparticles (grain size ~ 20 nm) (Figure S2c,d). This wrinkled topography significantly increases the effective surface area of the electrode by a factor of 5. The ratio of effective surface area to geometrical area can be estimated by the ratio of the length of the wrinkled surface profile to that of corresponding bottom straight line (Figure S4). Higher effective surface area lowers the interfacial impedance when the electrode is used to detect bio-electric signals.^[69] The wrinkled structure also contributes to the stretchability of the film. During stretching, initial cracks appeared at the depression positions (**Figure 3a**) from where they propagated further. Some upheaval blocks twisted and kept connected (inset of Figure 3a, and Figure S5), maintaining electronic pathways.

It should be emphasized that wrinkles seen here are different from those fabricated by the conventional pre-stretch method.^[70-72] For the pre-stretch method, 2D pre-strain is applied to the elastic substrate before metal film deposition and maintained constant during deposition (Figure S6a). When the pre-strain is released, a 2D pattern appears due to the mismatch of the moduli. The amplitude of these wrinkles is highly dependent on the thickness of the metal film and its adhesion to the substrate. If the thickness of the metal film is too large (like ~ 300 nm), it is difficult to form a regular and dense wrinkled structure according to the buckling theory.^[70] Our experiments show that there are wrinkles for a 300 nm thick gold film (Figure S6b) and that wrinkles still exist for gold films as thick as 500 nm prepared by the 3D diffusion process (Figure 2e,f). Besides, the typical characteristic of the stretchable film fabricated by the pre-stretch method is that the whole film becomes tortuous when the film is released from the pre-stretch condition (Figure S7a,b), although the thickness

of this PDMS substrate is $\sim 500\ \mu\text{m}$ which is much larger than that of the deposited gold film ($\sim 300\ \text{nm}$). This tortuous film is not only difficult to be further manipulated for the electrode preparation, but also hard to be used in the application. Additionally, when releasing, there would be a tensile strain applied to the gold film in the direction perpendicular to the pre-stretch one due to the Poisson effect. Long cracks are induced in this direction (Figure S7c) which would cause problems for the subsequent fabrication. By using our proposed deposited method, the film is flat without these phenomena (Figure S7b).

The stretchability achieved by our interlocking films was up to 130% (Figure 3b, Figure S8 and Supporting Video 2). While for the gold film with same thickness of 300 nm deposited by the conventional method, it possessed throughout cracks upon the mechanical tensile strain of around 10% (Figure 3b and Figure S9). So the stretchability of TRAP film was much better than that of conventional deposition. We further studied the effect of gold film thickness on stretchability (Figure 3c). When the film thickness increases, surface wrinkles are gradually filled up. Moreover, the number of defects inside the film increases with thickness and lowers its ductility. The stretchability decreases again upon further increasing the film thickness (Figure 3c). Thin film samples subjected to 10,000 strain cycles at 60% strain performed excellently (Figure 3d). Furthermore, the adhesion between gold film and polymeric substrate is vital for the real application of stretchable electronics. We obtained an adhesion strength of 2 MPa for a film conductor prepared by the semi-polymerized PDMS method (Figure 3e). This is significantly higher than the corresponding value obtained for gold film deposited on fully polymerized PDMS ($\sim 0.5\ \text{MPa}$). The fracture strength of PDMS film under tensile strain is around 2.2 MPa,^[73] whereas the adhesion strength of our TRAP film reaches similar values, indicating that the adhesion strength approaches the theoretical limit. Such strong adhesion is achieved through the interlocking process as discussed before. The gold atoms strike into the semi-polymerized PDMS and connect it with the substrate (inset of Figure 2d). In order to intuitively demonstrate the

adhesion enhancement, we employed high-adhesion Kapton tape and performed a peel-off test (Figure S10 and Supporting Video 3). It is clearly shown that the high-adhesion Kapton tape made little damage to our TRAP film but peeled off a large area of gold from conventional stretchable gold film and non-stretchable gold film. We also investigated the effects of cross linker to monomer ratio and pre-curing time on adhesion and stretchability, and found that the optimal preparation condition is ~ 25 -min pre-curing at 60 °C at a cross linker to monomer ratio of 1:5 (Figure 3e,f).

Considering the simple fabrication process, the superior performance and large-scale yield (Figure 2a and Supporting Video 1), our stretchable conductor would be a suitable candidate for stretchable electrodes, soft sensors and other flexible electronics devices. As a proof of concept, we used our stretchable conductor for on-skin electromyography (EMG), skin surface deformation and *in-vivo* applications. One of the treatments to nerve damage is targeted muscle reinnervation (TMR), i.e. transplanting a nerve to the targeted muscle to build a new connection (**Figure 4a**). In this treatment, our stretchable conductors can be applied to monitor the function recovery of affected muscles in two ways: 1) concurrent monitoring of on-skin EMG and related skin surface deformation; 2) *in-vivo* monitoring of intramuscular EMG (Figure 4a). For the on-skin route, we adhered encapsulated electrodes (Inset of Figure 4b) to the skin of a normal person and a disabled person, respectively (Figure 4b). Next, the participant was asked to pose different hand gestures, and the EMG and strain signal were recorded simultaneously, showing good synchronism (Figure 4b and Supporting Video 4). Traditionally, EMG is the most common signal to characterize hand gestures in TMR. Here, our results show that skin deformation also can be used to recognize the gestures with comparable accuracy (Figure 4c), and when combined with on-skin EMG, the overall accuracy was further improved, especially for the disabled person (Figure 4c). For *in-vivo* testing, our electrodes were implanted in rats to collect the intramuscular EMG signals (Figure S11 and Figure 4d,e), which were transmitted to the signal processing unit through a

home-made wireless transmitting module. The implantation and mounting operation did not affect daily movements of the rat (Supporting Video 5 and 6). EMG signals collected in such way display low noise as verified by the spectrum analysis (Figure 4e). Additionally, monitoring of signals over a four-month period was successfully conducted and the first-month impedance between the two electrodes were recorded, showing only a little increment with an obvious fluctuation (Figure 4f). The scattered natures of the impedance should be induced by the movement of rats during the monitoring. The rat can freely walk and the distance between the implanted electrode and muscle changed from time to time. Besides, the impedance test shows that the high active area of TRAP film brought about lower impedance compared to the traditional film (Figure S12a,b). It significantly benefited the bio-signal detection. All these application experiments show that our stretchable electrodes can work reliably for both on-skin and *in-vivo* applications. Following this work, many other biomedical problems could be addressed using the developed electrodes. For example, we successfully demonstrated that our stretchable conductors can be utilized as neural stimulators to efficiently drive the movements of thigh muscles in rats (Supporting Video 7 and 8), showing potential for neural regeneration and rehabilitation (Supporting Note3, Figure S12,13). In addition, electrode patterning is important for electrode array preparation and multichannel signal detection. For TRAP film, the shadow mask can be used during the metal deposition to prepare patterns. Also, the semi-polymerized PDMS would not be fully polymerized due to the shielding of mask and much less heat receiving from the heat radiation. The post-heating would be needed to further polymerize the PDMS. Besides, the shadow mask surface adhered to the semi-polymerized PDMS should be prepared with fluoridation or by other hydrophobic treatments, in order to be easily peeled off after the full polymerization of PDMS.

In summary, we report a new strategy, metal interlocking, with a new approach of thermal radiation-assisted metal encapsulation (TRAP) to fabricate highly stretchable and

stable stretchable conductive films. Through this interfacial design approach, thin-film conductors with high stretchability and cyclic stability, high interfacial adhesion and large active surface area can be realized. Additionally, such conductors can be easily fabricated in a large scale with a readily accessible method, and the only key issue is to use semi-polymerized PDMS as the substrate for gold thermal deposition. The conductor is applied to monitor both mechanical deformations and *in-vivo/-vitro* electrophysiology signals. It can also act as an implantable nerve stimulator to benefit neural regeneration/rehabilitation. Our proposed strategy highlights the critical role of conductive film-substrate interface in stretchable thin-film conductors and paves the way for the exploration of high-performance stretchable conductors based on interfacial design. The reported stretchable conductor undoubtedly offers huge potential for practical application in the field of implantable soft electrodes, body-surface electrophysiology signal harvesting and other stretchable smart sensors. As the basic unit for stretchable devices, stretchable conductors offer solid support for the development of future stretchable electronics.

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Figure 1. Thermal radiation-assisted metal encapsulation (TRAP) of gold and polymer at the interface to tune the strain distribution in metal film and enhance the interfacial adhesion. a) Diagram to show the cross-section view of the neat metal film on substrate and metal film with interlocking interface to the substrate. Below panels show the front view of the simulation result of mechanical strain distribution in metal film for both cases when the tensile strain of 30% is applied to the sample. The strain is calculated by using finite element modeling method. b) Adhesion strength can be enhanced by increasing the contact area according to the theoretical prediction.^[68] c) Strain distribution comparison of one monitoring line (black dashed line in b)). Compared to the flat film without interlocking interface, the film with interlocking one has more discrete strain concentration. This strain concentration results in discrete micro fractures in the metal film and offers thereby high stretchability. d) Diagram to show of thermal radiation-assisted metal encapsulation (TRAP) in semi-polymerized PDMS, including stage 1: metal diffusion, stage 2: continuous polymerization, and stage 3: metal encapsulation. The physical model related to the heat transfer is illustrated in Figure S1, and the detailed analysis of the heat transfer is in Supporting Note 1 and 2.

Figure 2. Structural features of the TRAP film. a,b) Optical images of the large-scale TRAP film in front view in a) and reverse view in b). c,d) Cross-section SEM images to show the structural feature at the interface. Inset image in d) shows the interlocking interface by the diffusion of gold into semi-polymerized PDMS and then fully cured assisted by thermal radiation. e,f) SEM and AFM images of the gold film showing the wrinkled structure with upheaval and depression.

Figure 3. Performance of the stretchable conductor. a) SEM image of the stretchable film under tensile strain of 50 %. Inset shows the connecting bridge by the upheaval twisting. b) Resistance change of the TRAP film and neat film. It is out of the measurement range indicating the gold film break. Inset presents the optical image of the testing process. c) Maximum stretchability affected by the deposition thickness. d) Resistance change under cyclic tensile strain to show the stability of the stretchable conductor. e,f) Adhesion strength and maximum stretchability with different precursor-to-monomer ratio and pre-curing time.

Figure 4. Demonstration of the TRAP film as the bio-interface sensing electrode for targeted muscle reinnervation. a) Illustration image to show the targeted muscle reinnervation. In order to quantitatively monitor the muscle reinnervation, there are two levels of monitoring including on-skin detection and intramuscular one. For on-skin one, we applied our sensors to human directly, while for the latter one, an animal model was used. b) Optical images to

show the encapsulated sensors by using our novel electrodes (inset in top left panel), and the sensor was applied to simultaneously detect on-skin EMG signal and surface deformation of the normal subject and disabled subject (bottom left panel). Experimental data from the synchronous monitoring of EMG signal and deformation signal (right panel). c) Motion recognition accuracy depending on different detected signals. d) Images to show long-term implantation testing of animal model for intramuscular monitoring. Wireless data-acquisition system integrated with the rat (left panel), nerve bundle transplantation process (middle panel) and our novel electrodes applied to detect the signal (right panel). e) Intramuscular EMG signals detected and related spectral analysis. f) Electrode impedance monitoring in one month after electrode implantation.

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A new strategy of thermal radiation-assisted metal encapsulation is reported to prepare large-scale high-performance stretchable conductors, which possess high stretchability, stability, high adhesion and high surface area. They are used to simultaneously monitor EMG and skin deformation and implanted to detect intramuscular signals. Our study offers a new path for highly-stable stretchable conductors and related bio-interface applications.

Keywords: stretchable conductors, interlocking effect, polydimethylsiloxane, adhesion, stability

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Highly Stable and Stretchable Conductive Films through Thermal Radiation-assisted Metal Encapsulation

ToC figure