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Highly Stretchable Compliant Polymeric Microelectrode Arrays for In-vivo Electrophysiological Interfacing

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Abstract:

Polymeric microelectrode arrays (MEAs) are emerging as the new generation of bio-integrated microelectrodes to transduce original electrochemical signals in living tissues to external electrical circuits and vice versa. So far, the challenge of stretchable polymeric MEAs lies in the competition between high stretchability and good electrode-substrate adhesion. The larger the stretchability, the easier the delamination of electrodes from the substrate due to the mismatch in their Young's modulus. In this work, by inducing the wavy structure and a nanowire-based transition layer to the electrodes, for the first time, we fabricated stretchable

polymeric MEAs with both high stretchability (~100%) and good electrode-substrate adhesion (1.9 MPa). In addition, low Young's modulus (450 kPa), excellent recycling stability (10,000 cycles of stretch) and high conductivity of the MEAs were also achieved. As a proof of concept, the as-prepared polymeric MEAs were successfully used for conformally recording the electrocorticograph (ECoG) signals from rats in normal and epileptic state, respectively. Further, these polymeric MEAs are also successful in stimulating the ischiadic nerve of the rat. Our strategy provides a new perspective to the high stretchable and mechanical stable polymeric MEAs which is vital for compliant neural electrodes.

Microelectrode arrays (MEAs), which interface living tissues with electrical hardware, constitute powerful tools for the transduction of original electrochemical signals in living tissues to electron-based currents in external electrical circuits, and vice versa.^[1-5] Through these recording and stimulating processes, MEAs play a vital role in promoting the understanding of underlying physiological mechanisms, as well as improving diagnostics and therapy of neurological disorders and disabilities.^[6-12] In recent years, conducting polymers have witnessed great progress in the design and fabrication of *in vitro* and *in vivo* MEAs for bio-integrated electronics.^[13] The conductivity of conducting polymers results from the delocalization of electrons in the overlapping carbon orbitals along the polymer backbone and the existence of mobile charge carrier (dopant) moving along the π -bonded carbon atoms.^[14-16] therefore the conducting polymers can transfer charge both by electronic and ionic mechanisms which greatly reduced impedance.^[17] Furthermore, comparing to the inorganic counterparts, conducting polymers hold many advantages for serving as MEAs materials, such as facile solution-based fabrication, diminished foreign-body response, low costs, greatly reduced impedance, as well as

good stimulation capacities.^[18-22] Typically, conducting polymers serve as coating layers for the modification of metallic electrodes,^[23-25] thus efficiently lowering the electrode-tissue impedance and synchronously propelling electron transportation owing to the high conductivity of the metals.^[18, 26] However in these conducting polymer-metal composite MEAs, drawbacks associated with their noble metal parts should be addressed, such as high rigidity, possible invasion to tissues, relatively high costs and poor stretchability. Furthermore, the possible delamination of the conducting polymer coating constitutes an important factor that needs to be considered.^[27] These critical issues result in the major challenges that lie ahead in this field.

Polymeric MEAs, which employ conducting polymers as the sole conductors, play an important role in the growth of next-generation bio-integrated electronics, as they provide a more promising route for achieving cost-effective and intimate biotic/abiotic interfaces.^[28-30] A key performance parameter of the polymeric MEAs is their compliant feature which enhances their compatibility with the soft biological tissues. Here, the compliant feature refers to two factors; the first is the conformal match of the electrode-tissue interface, as shown in **Figure 1a**. Many works that focus on conformal electrode-tissue interface have been reported.^[31-35] However, two more crucial features are still indispensable for conformal electrode-tissue interface. (1) high stretchability of MEAs is demanded to satisfy the strain induced by the living tissues (10% strain for brain, 20-35% strain for heart and ~ 100% strain for skin),^[36] and (2) low Young's modulus is required to enable easy stretching of the MEAs in the biological system.^[37-42] The second factor is the good adhesion of the electrode-substrate interface (Figure 1a), in order to avoid the detachment of electrodes from the substrate during numerous cycles of stretching induced by the tissues. Recently, the first stretchable polymeric neural MEAs were demonstrated using Polypyrrole/polycaprolactone-block-polytetrahydrofuran-block-polycaprolactone composite

films as the sole conductors. These MEAs showed a Young's modulus of 153 ± 25 MPa and could withstand 7.5 stretching/relaxing cycles at $\sim 22\%$ strain without obvious increase in resistance. Furthermore, it showed a reduced impedance that is far better than that of the metal-based MEAs.^[43] However, the research on stretchable polymeric MEAs is still at the embryonic stage, highly stretchable compliant polymeric MEAs are still urgently desired for the bio-integrated electronics. The crucial challenges to this goal lie in the competition between the electrode-tissue interface and the electrode-substrate interface. High stretchability and low Young's modulus would contribute to a conformal electrode-tissue interface. However, they would also easily results in the detachment of electrode materials from the substrate due to the large strain induced and the mismatch of Young's modulus. As a result, a poor electrode-substrate interface is inevitable. Therefore, the main challenge for high stretchable compliant polymeric MEAs is the achievement of both high stretchability and good electrode-substrate adhesion.

In this work, by introducing a transition layer to the wavy structured electrode arrays, we have successfully fabricated highly stretchable compliant polymeric MEAs, where only polypyrrole (PPy) serves as the conductive electrode. The as-prepared MEAs can provide both good electrode-tissue interface and high adhesive electrode-substrate interface, because the devices not only possess an high stretchability (100% strains) and low Young's modulus of ~ 450 kPa, but also show enhanced adhesion between the electrode arrays and substrate (~ 1.9 MPa). In addition, it could withstand 10,000 cycles of mechanical loading and exhibit a conductivity of ~ 800 S/cm which is much larger than the previous reported polymeric MEAs.^{[25,}
^{43]} Not only that, good electrochemical stability of the MEAs was also achieved. As a proof of concept, we demonstrate the successful *in vivo* pathological application of the polymeric MEAs

by conformally recording the electrocorticograph (ECoG) signals from rats in normal and epileptic states, respectively. Furthermore, these polymeric MEAs are also successful in stimulating the ischiadic nerve of the rat. Our strategy provides a new perspective to the high stretchable and mechanical stable polymeric MEAs which is vital for compliant neural electrodes.

One effective way to make stretchable electrodes is to induce wavy structure to the electrode materials by a pre-stretching strategy.^[44-45] In this work, we also employ this strategy to fabricate the stretchable polymeric electrodes, as shown in Figure 1b. Here, the wavy structure not only enables the electrode to be highly stretchable, but also enables the whole MEAs device with a lower Young's modulus compared with that of the MEAs with flat electrode structures. Therefore, it is much easier to stretch the MEAs based on wavy structured electrodes. Additionally, the wavy structure induces less strain to the electrode during the stretching/relaxing process (Figure 1c), thus, these electrodes are expected to maintain good recycling stability.^[36, 46] However, a severe problem of the wavy structured electrode is the delamination of the electrode materials from the substrate, because the adhesive force normally comes from the weak Van der Waals' interaction. Furthermore, the decreased electrode-substrate contacting area resulting from wavy structures make the adhesive force much weaker. This problem is even more critical when a high stretchability is required. Here, inspired by the buildings which stand firmly on the ground by a transition layer (taking foundation in the soil), we can build a transition layer (nanowires buried in the substrate materials) at the electrode-substrate interface to enhance the adhesion between the electrode arrays and substrate (Figure 1b). Hence, the delamination of the electrode arrays from the substrate can be dramatically suppressed. As depicted by the simulation results in Figure 1d, compared with the electrodes without nanowire modification (Figure 1d-2), the adhesive strength of nanowire modified

electrodes can be dramatically enhanced (Figure 1d-1 and 1d-3) (more details of the calculation can be found in Figure S1 in Supporting Information). Furthermore, because the transition layer enhances the electrode-substrate adhesion, it may also facilitate the transfer of electrode arrays to the substrate materials during the fabricating process.

In a typical experimental process, to achieve the proposed wavy structured electrodes with transition layer at the electrodes-substrate interface, we designed a reliable and facile “stamping transfer method” for the fabrication. As schematically shown in **Scheme 1**, the PPy electrode arrays were first deposited on the pre-patterned ITO slide by electropolymerization (more details can be found in Supporting Information and the setup is schematically shown in Figure S2). PPy has alternating single bonds and double bonds (π bonds) in the polymer backbone, as the molecule structure shown in Figure S3. It exhibits good electrical conductivity, good biocompatibility and has been widely used in the tissue engineering.^[47,48] To avoid the delamination of PPy electrode from the PDMS substrate due to their mismatch in Young’s modulus, we fabricated a layer of PPy nanowires on the PPy electrode to enhance their adhesion. The enhanced adhesion not only improves the mechanical stability of the MEAs, but also facilitates the transfer of PPy electrodes to the PDMS substrate. PDMS is one kind of silicon-based organic polymer with a structure containing carbon and silicon (Figure S3). It is widely used in medical devices due to its inert, non-toxic and biocompatible properties. After removing the photoresist, a “stamping transfer method” was conducted to transfer the PPy electrode arrays. In this process, we stamped the PPy electrode arrays onto pre-stretched PDMS substrate. It should be pointed out that a thin layer of semi-cured PDMS was coated on the substrate’s surface to serve as glue (the total thickness is about 160 μm , Figure S4). Due to the transition layer where PPy nanowires take root into the thin PDMS layer, the electrode-substrate adhesion is

greatly enhanced. Thus, after peeling off the ITO slide, the PPy micro-belts were uniformly transferred to the pre-stretched PDMS substrate. By releasing the substrate, a highly wavy structured PPy electrode arrays grasping tightly on PDMS substrate was obtained. Till date, several strategies have been reported for the fabrication of stretchable electrodes.^[46, 49] However, these fabrication processes are complicated and unreliable for the fabrication of polymeric MEAs, whereby the electrodes are often subjected to harsh solvents or high-energy fields, resulting in unstable electrical properties.^[24] The decrease in conductivity of the as-obtained material is primarily due to its tendency to de-dope again in biological environment (Figure S5 in Supporting Information). For our design, it was ensured that, during the entire fabrication process in our design, PPy conductors are free from exposure to harsh solvents and high-energy fields, resulting in enhanced electrical stability (Figure S5).^[43]

The inherent mechanical properties have a great effect on the performance of the compliant polymeric MEAs. The stretchability of the polymeric MEAs was first checked through simple visual clues. Specifically, we fabricated a multielectrode array with tens of PPy micro-belts on a pre-stretched (100%) PDMS substrate (**Figure 2a**). Subsequently, we designed a simple circuit to power a LED lamp, in which the PPy micro-belts were employed as a stretchable conductor. The LED retained its luminescence when the PPy micro-belts were stretched to a strain of ~100%, indicating that the MEAs had stable electrical conductivity under stretching. To further investigate the mechanism of the observed electromechanical behavior, the surface morphology of the PPy micro-belts was monitored in-situ during a stretching/releasing cycle via optical microscopy (inset of Figure 2b and 2c). It was observed that the PPy micro-belts remained tightly adhered to the PDMS substrates during the whole stretching process. In released state, wavy PPy micro-belt structures were induced due to

buckling in the stretching direction. By increasing the strains on samples, the amplitudes of these wavy structures reduce with a corresponding increase in their lengths. Even when the strain increased to the original pre-stretched length of $\sim 100\%$, no crack was observed on the PPy micro-belts, which accounts for the excellent electromechanical stability. In contrast, when metal is employed as the conductive electrode, such mechanical performances cannot be obtained. A control experiment was conducted by fabricating gold micro-belts on a pre-stretched PDMS surface via an etching-assisted transfer method (60% pre-stretched length).^[36] As shown in Figure S6, after the pre-stretch is released, many cracked regions appear within the gold belts. This is because, during stretching/releasing process, the stresses along various directions produced by the PDMS damage the fragile metal electrodes easily. While the PPy conductors possess a 154.5 MPa tensile strength and can inherently withstand tensile strains of $\sim 9\%$ (Figure S7), indicating their remarkable mechanical strength.^[43, 50, 51] Therefore, such high stretchability of the as-prepared polymeric MEAs should be ascribed simultaneously to the excellent inherent mechanical properties of the PPy conductors and the wavy micro-structures. Concurrently, the electrical properties of the PPy micro-belts were further in-situ characterized during stretching. Figure 2d shows the I-V curves subjected to varying strains, indicating that these highly stretchable polymeric MEAs could be easily stretched up to a strain of 100% (100% is the pre-stretched length) without any increase in resistance. Moreover, the stability of the polymeric MEAs was tested by recording its resistance during 10,000 cycles of the stretching/relaxing processes and no obvious increase in resistance was observed (Figure 2e). The resistance of the MEAs at different strains was also measured after conducting 10,000 stretching/relaxing cycles. The result shows that the polymeric MEAs still keep stable conductivity under different strains (Figure 2f). The Young's modulus of the as-prepared MEAs is ~ 450 kPa (Figure S8), which is

much smaller than that of the bare PPy electrode (154 MPa) (Figure S7). Thus, compared to the MEAs based on flat PPy electrodes, the as-prepared compliant polymeric MEAs is much easier to be stretched in the biological system. Furthermore, to demonstrate the advantages of reducing the Young's modulus of MEAs, we pasted the as-prepared MEAs on the wrist. As shown in Figure 2g, the device adhered to skin very well, and can be easily stretched by the adhesive force between PDMS and human skin (Video S1). In contrast, when the flat PPy film on a PDMS substrate was pasted to the skin in the same way, it is too stiff to be stretched, owing to its high Young's modulus (Video S2). These results demonstrate the excellent mechanical properties of the as-prepared compliant polymeric MEAs.

One particular problem of the stretchable compliant polymeric MEAs comes from the electrode-substrate interface, which is the detachment of the electrode materials from the substrate during the stretching/relaxing process due to the mismatch of their Young's modulus. To enhance the electrode-substrate adhesion, we synthesized nanowires on the surface of PPy electrode to construct the transition layer. As shown in Figure 2h, the PPy nanowires uniformly cover the surface of PPy electrodes. The nanowires can be buried in the semi-cured PDMS layer on the substrate. After complete curing, the nanowires were immobilized firmly in the PDMS substrate (Figure S9). Therefore, the electrode-substrate adhesion is greatly enhanced. As shown in Figure 2i, the adhesive strength increase to about 1.9 MPa after nanowires (aspect ratio is ~ 10) modification (~ 0.25 MPa without nanowires modification) (The details about the setup of the adhesive strength measurement is shown in Figure S10). Furthermore, the adhesive strength of the PPy film with different aspect ratio were compared (Figure S11), the adhesive strength increased with the increase of aspect ratio of the nanowires which is in consist with the simulating results. To demonstrate the enhanced adhesion in a visual way, we pasted the high

temperature tape (acrylic adhesive, product of 3M Company) on the top of PPy film, where nanowires were modified on its bottom side, and buried in the PDMS substrate (Figure S12a and S12b). The PPy film adhered to the PDMS substrate too tightly to be removed by peeling of the tape (Video S3). Contrastingly, without the modification of nanowires, it can be easily removed by the tape, as shown in Figure S12c, Figure S12d and Video S4. Additionally, it has been well confirmed that, the smaller the material thicknesses, the better it matches with the substrates.^[24, 31] In our work, the thickness of PPy electrodes has been decreased by one to two orders compared with their previous counterparts used in MEAs.^[30, 43] The thin structure enables the PPy electrode to exhibit excellent flexibility, as shown in Figure S13. It can be easily bent with a radius of curvature typically less than 100 μm . To highlight the benefits of reducing the electrodes' thickness, we conducted experiments figuratively by putting the PPy films with different thicknesses on the back of the hand, as shown in Figure S14. The crease details of the hand can be clearly observed permeating through the 1.5 μm -thick PPy conductors, indicating that a conformal cover on a curvilinear surface can be achieved. Contrarily, for the control sample with a thickness of ~ 15 μm , the PPy film is too stiff to provide a fitting contact. Therefore, the reduced thickness of the electrodes enables them to match the surface of substrate, and nanowires based transition layer greatly enhance the adhesion of electrode-substrate interface.

It has been well established that the improvement in electrical conductivity of conducting polymers can dramatically enhance the charge transfer of polymeric MEAs for neural interfacing.^[18] One way to improve the conductance of the polymeric electrodes is to increase their thickness.^[43] However, this high thickness tends to passively increase their stiffness, which influences the match of electrode-substrate interface.^[31, 52] Otherwise, these stiff electrodes act

as micro-knives in the soft biological system which result in the injury of brain and neural fibers.^[53] In this work, we employed aqueous p-toluenesulfonic acid (PTSA) as the electrolyte instead of the conventionally used sodium p-toluenesulfonate (PTS-Na) to improve the conductivity of the PPy electrode (More details can be found in the experimental part). The impact of the synthesis conditions on conductivity of PPy was investigated and characterized by the standard four-point probe method. It is found that the current density exhibits insignificant effects on the conductivity of the PPy electrode. As shown in Table S1, when a current density of 0.5 mA/cm² is applied, PPy exhibits the highest conductivity. So 0.5 mA/cm² is chosen as the standard electroplating current density for all the experiments in this work. The samples polymerized in PTSA solution exhibit remarkably higher conductivity than that of PPy prepared in PTS-Na electrolyte (Figure 3a). In particular, when the mole ratio of pyrrole (py) : PTSA is 1:2, the PPy film shows the highest conductivity of 820 S/cm, which is much larger than the previous reports.^[25, 43] To reasonably explain this result, we take both inter-chain and intra-chain conductivities of the conducting polymers into consideration. In many cases, the inter-chain conductivity of p-conjugated polymers play a vital role in the macroscopic conductivity due to the significant barrier between the polymer chains.^[22, 54, 55] The vivid metallic luster of the PPy films represent a high electron density per unit volume (Figure S15a).^[54] In addition, the PPy films show smooth surfaces composed of nanosized particles (Figure S15b), implying a low electrical resistance in the films obtained.^[54] This suggests that the PPy films may have a high inter-chain conductivity. We also characterized the molecular structure of the as-prepared PPy by Raman spectra (Figure S16) for quantitatively estimating the conjugation length, which determines the intra-chain conductivity. The intensity ratio of Raman peaks corresponding to the symmetric C=C stretching mode (1580 cm⁻¹) and the skeletal band (1500 cm⁻¹) of the PPy film

synthesized in PTSA solution is larger than that of the PPy film fabricated in PTS-Na solution, which strongly indicates the lengthening of the π conjugation of the PPy chains.^[56, 57]

Most of the information processed and transmitted in the biological nervous system is of electrochemical nature, and the transferring efficacy of the electrical signals between ions and electrons at the electrode-tissue interface plays a vital role in the performance of MEAs.^[4, 11] Accordingly, the electrochemical properties of our polymeric MEAs were characterized in phosphate buffer saline solution (pH = 6.8). A gold electrode with the same geometric size (~150 nm thickness) was employed for a fair comparison. As the electrical impedance spectroscopy shown in Figure 3b, polymeric MEAs show a much better response than those of the gold electrodes at lower frequencies (below 100 Hz). In addition, the phase responses (Figure 3c) indicates that the PPy electrodes are more resistive at frequencies below 1 kHz.^[7,8] The as-prepared polymeric MEAs are expected to be more suitable for recording local field potentials (1 Hz ~ 100 Hz). The function of electrode-tissue interface is to realize effective communication between bio-system and external electrical systems. Aside from recording of electrophysiological signals from the bio-system, the transfer of external electrical signals into the bio-system is equally important.^[58] The external input electrical signals not only can stimulate the bio-system for treatment of diseases, but also serve as a continuous feedback for the neural prosthesis.^[59] To characterize the stimulation capability of our polymeric MEAs, we employ cyclic voltammetry (CV) sweeps to demonstrate its charge storage capability at low scan rate (50 mV/s, Figure 3d) and high scan rate (1 V/s, Figure 3e), respectively. Our MEAs show a capacitance of ~ 67.1 mC/cm² at a scan rate of 50 mV/s (Figure 3f), which is one of the best figures achieved so far in the polymer-based electrodes.^[23, 60] This value is an order magnitude higher than that of smooth gold electrode (1.4 mC/cm²). At high scan rate (1 V/s), the polymeric

MEAs still possess a capacitance of 5.3 mC/cm^2 , while that for the gold electrode is 0.2 mC/cm^2 (Figure 3f). As discussed above, the inherent mechanical properties and excellent electrical properties suggest that our highly stretchable polymeric MEAs are outstanding candidates for bioelectronic applications.

Eventually, facilitated by the mechanical and electrochemical properties of the polymeric MEAs, we demonstrate them as practical implants for the *in vivo* identification of normal and epileptic rat through the recording of ECoG signals. The tests here involved an anaesthetized rat with its head (with $4 \times 5 \text{ mm}$ exposed region of cortex) fixed in a stereotaxic apparatus. The as-prepared MEAs (**Figure 4a**) were merely used to cover the visual cortex as shown in Figure 4b. Figure 4c and Figure 4d show the four channel ECoG signals when the rat was in the normal (Figure 4c) and epileptic (Figure 4d) state, respectively. The sudden intensified brain signals in the epileptic rat could be clearly and obviously observed using our polymeric MEAs. Cloud maps of the alpha wave band (8-14 Hz), extracted from four-layer decomposition of the first channel using functioned waves and db10 wavelet were also used to analyze the ECoG. A sharp increase in energy appears in 10.5-11.5 Hz, which is caused by the brain synchronicity discharge induced by epilepsy. Furthermore, encouraged by the high charge storage capability (67 mC/cm^2) of the polymeric MEAs, we demonstrate the stimulation efficiency of the MEAs by *in vivo* stimulating the ischiadic nerve of the rat. As shown in Figure 4e, the MEAs wrap the neural fiber well and form a conformal contact with it. The polymeric MEAs were used to deliver pulsed electrical input to the neural fiber such that the rat leg moved periodically (video S5), and the corresponding electromyography (EMG) was recorded by the needle electrodes (Figure 4e and Figure 4f). It is noteworthy that even after 200 electrical pulse stimulations (0.6 Hz current pulse, ms pulse width), no obvious fatigue in the rat leg was observed (Figure S17). This

accounts for the enhanced electrochemical stability and long term functionality of the polymeric MEAs. Otherwise, the good bio-compatibility and bio-safety of the PPy electrode can be evaluated by the high viability of the cells on the surface of PPy electrode (Figure S18) and the normal status (no obvious inflammation was observed) of the tissue around the implanted electrode after one week implantation (Figure S19). The as-prepared PPy electrode also exhibited good long-term stability both in mechanical and electrical properties (Figure S20). Due to its facile fabrication, low cost, as well as its efficiency in neural interface electronics, the highly stretchable PPy-based polymeric MEAs constitute promising candidate for *in vivo* neural interfacing applications. It is believed that the present work can promote the development of polymeric bioelectronics for practical applications.

In conclusion, by introducing wavy structures and transition layer to the electrodes, we successfully fabricate highly stretchable compliant polymeric MEAs for electrophysiological interfacing. Firstly, the compliant polymeric MEAs provide a conformal match of electrode-tissue interface. This is contributed by the merits of high stretchability (no electrical conductivity changed under 100% uniaxial tensile strain) and low Young's modulus (~ 125 kPa), of the polymeric MEAs. Secondly, the compliant polymeric MEAs possess enhanced electrode-substrate adhesion (~ 1.9 MPa), which is contributed by the transition layer. Additionally, excellent recycling stability (10 000-times repeated mechanical loading), high conductivity (exceeding 800 S/cm) and stable electrochemical properties were also achieved. As a proof of concept, we demonstrate a successful implementation of using the as-prepared polymeric MEAs for *in vivo* recording the ECoG signals from the rat in normal and epileptic state respectively. Further, these compliant polymeric MEAs were also successful in stimulating the ischiadic nerve

of the rat. Our strategy provides a new perspective to the high stretchable and mechanical stable polymeric MEAs which is vital for compliant neural electrodes.

Supporting Information

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

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Figure 1. (a) Schematic draw of the compliant electrode arrays adhering on brain, the enlarge draw shows more details about the electrode-tissue interface and electrode-substrate interface, respectively. (b) Proposed concept to achieve high stretchability and strong substrate adhesion. A drawn of the inspired highly stretchable electrode with enhanced substrate adhesion. Here, the wavy structures provide stretchability and transition layer (nanowire & substrate materials)

enhanced the adhesion between the electrode and substrate. (c) Finite element method (FEM) stimulation result of the strain distribution on the (1) wavy structure, (2) flat structure on elastic substrate and (3) the peak stress comparison of wavy and flat structures with different strains. (d) FEM simulation of the stress distribution in the film (1) with cylinders (2) without cylinders and (3) the proportion of adhesion stress (film with cylinders/flat film) at different aspect ratio of the cylinders.

Scheme 1. The scheme for the fabrication of the fully-polymeric microelectrode arrays. (a) the fabrication of photoresist pattern on ITO glass via a photolithography process. (b) Deposition of PPy film on the exposed ITO surface by electro-polymerization. (c) Synthesis of PPy nanowires on the surface of PPy film (inset is a magnified scheme). (d) PPy electrode on ITO surface (The photoresist was removed). (e) The pre-stretched PDMS thin film was covered on the PPy electrode surface, after casting a layer of half-cured PDMS. (f) The stretchable all-polymeric electrode arrays was produced after fully curing of the PDMS and peeling off the electrode from ITO glass (inset is a magnified scheme of the PPy nanowires buried in PDMS substrate.).

Figure 2. (a) Optical images of the multi-electrode array. A LED illuminated by using a multi-electrode array as the connecting wire under (b) no strain, (c) 100% strain and inserts are their optical microscopy images of PPy micro-belts, respectively. (d) I-V curves of the stretchable array with different strains. (e) Comparison about the resistance of electrode arrays after different stretching/relaxing cycles (R) with its initial value (R_0) (f) resistance of the electrode arrays with different strains after stretching/relaxing 10 000 times, which were recorded at 0.5 V. (g) Digital photo of the all-polymeric electrode pasted on the wrist and after being stretched (25%). (h) Optical images of the multi-electrode array on ITO glass (left) and SEM image of the PPy

nanowires synthesized on the PPy electrode surface (right). (i) Adhesion comparison of the PPy films with nanowires modification and without nanowires modification.

Figure 3. (a) The conductivities of various PPy films fabricated by different electropolymerization conditions (1:1, 2:1, 3:1 of pyrrole (py) : PTSA ratios and 2:1 of pyrrole (py) : PTS-Na ratio). (b) (c) Electrical impedance spectra of the PPy film and Au film electrodes with the same geometric surface area as a control. (d), (e) Cyclic voltmmetry (CV) curves of the PPy electrode and gold electrode at scan rate of 50 mV/s and 1 V/s respectively. (f) Charge storage capacities (Q_{cap}) of the PPy electrode and Au electrode at different scan rates (50 mV/s and 1V/s) of CV curves.

Figure 4. (a) Digital photo of the PPy electrode arrays. (b) A image of four-channels-MEA on the rat brain. (c), (d) ECoG signals of a normal and an epilepsy rat, the right parts are the corresponding cloud maps. (e) Digital image of a four-channels-MEA wrapped on the ischiadic nerve of a rat for stimulation and the two needle electrodes inserted in the leg of the rat for signal recording. The enlarged photo in right shows the MEAs conformally wrapped on the ischiadic nerve. (f) The inputed stimulating signals and the corresponding electromyography recorded.

Compliant polymeric microelectrode arrays (MEAs) with both high stretchability and enhanced electrode-substrate adhesion have been fabricated by taking the advantage of wavy structured electrode and nanowire-based transition layers. Additionally, good recycling stability and high conductivity were also achieved. Finally, the as-prepared stretchable polymeric MEAs were successfully implanted for neural recording and stimulation.

Keyword: stretchable electrode, electropolymerization, neural interface, microelectrode array, flexible devices

Highly Stretchable Compliant Polymeric Microelectrode Arrays for In-vivo Electrophysiological Interfacing

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ToC figure