Ultrahigh Skin-Conformal and Biodegradable Graphene-based Flexible Sensor for Measuring ECG Signal

Nan Wu, Hui Liu, Shu Wan, Shi Su, Haizhou Huang, and Litao Sun

***Abstract*—With the development of information technology as well as the arrival of the age of big data, researchers and engineers begin to pay attention to personal health data and biomedical electronics. At this time, real-time monitoring of the physiological signal of humans, such as electrocardiograph (ECG) signal, becomes vital to human beings. However, the traditional (Ag/AgCl) electrode has a couple of disadvantages such as poor stability, material waste, and heavy metal pollution. Here, our group has proposed a novel flexible ECG sensor, which is fabricated of graphene and polyvinyl alcohol (PVA) film via double transfer technique. In this electrode, graphene has been introduced as an active layer, while PVA film is served as a flexible electrode substrate. As a result, this whole sensor exhibits excellent mechanical and electrical properties and it can be biodegraded after use. The flexible sensor has a Young's modulus of 8.598 MPa, a maximum strain of 135%, and a resistivity of 35.88Ω·m. Additionally, its resistance fluctuated within 20% strain. Then, an ancillary signal processing circuit is designed for analog signal collecting from the flexible sensor. The digital signal processing system is programmed including analog digital converter (ADC), microprocessor, signal transmission, and mobile application software. In conclusion, the whole system achieves the measurement and display of ECG signal in real-time and offers a better solution for biomedical electronics in the future.**

***Index Terms*—Skin-conformal, biomedical electronics, real-time, wireless system, recyclable.**

I. INTRODUCTION

With the development of information technology as well as the arrival of the age of big data, people begin to pay attention to wearable technology, particularly biomedical electronics [1]. The development of different kinds of wearable flexible sensors is the cornerstone of this revolution [2]. With the assistance of various sensors, vital personal health data can be collected non-invasively and continuously [3]–[8] to build up a health database and improve medical diagnosis.

In addition, in the global scope, cardiovascular has gradually attracted extensive attention and the effective method to diagnose cardiovascular is electrocardiograph (ECG) signal. By monitoring the ECG signal in time, doctors can obtain information about the excitability of cardiac electrical activity and give necessary drug treatment. Therefore, it is of remarkable importance to use new technology and sensors to monitor ECG signal in real-time.

In recent years, there have been many breakthroughs in the field of flexible sensors, especially skin-conformal sensors [1]. The availability of flexible sensors, which were fabricated with polymers [9]–[12], nanowires [13], nanoparticles [5], [14], [15] carbon nanotubes [16], as well as graphene materials, *etc*., have led to devices with ultrahigh sensitivity and rapid response. These sensors are capable of detecting subtle signals in the human body such as sphygmus, vocal-cord vibration, and apical impulse. In addition, flexible sensors should also be biologically safe and can maintain a strong contact with skin. Especially the latter one, a strong contact with skin is important for the performance of the sensor and critical to the quality of signals [17], [18]. However, since human skin is relatively rough, it is difficult to obtain an ultra-conformal contact. In order to solve this problem, wound plasters have been widely applied. Although these flexible sensors show the capability to allow health monitoring, it could be potentially problematic due to incompatibility in flexibility between wearable sensors and tapes [1]. Once the adhesion of the tape to skin decreased during human motion, the performance of the flexible sensor would be deteriorated. Additionally, with the development of flexible sensors in recent years, how to handle these sensors' materials after using is an important problem. Most of the flexible sensors are made from materials (for example polydimethylsiloxane (PDMS)) that cannot be biodegradable after using and these would cause environmental pollution and material waste. According to recyclable principles, the best solution to deal with this problem is developing a biodegradable flexible sensor. Therefore, it is desirable to develop a facile strategy to create high-performance wearable sensors, which show ultrahigh skin-conformal adhesion and can be biodegradable after use.

Here, our group design and fabricate a novel flexible ECG electrode that is made of graphene and polyvinyl alcohol (PVA) film via a double transfer technique. Compared with previously reported techniques that require complicated fabrication process, the presented strategy is facile and exclude heating and etching processes. In this flexible sensor, graphene is introduced as an active layer and PVA film is served as a flexible electrode substrate. As a result, this whole sensor exhibits excellent mechanical (ultrahigh skin-conformal adhesion) and electrical properties (high signal-to-noise ratio) and it can be biodegraded after use. The flexible sensor has a Young's modulus of 8.598 MPa, which is similar to that of human skin, [1] and this mechanical property ensures the skin-conformal adhesion. Concerning ECG monitor characteristics, the variation of resistance of

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flexible ECG sensor should be inhibited. By applying the pre-stress structure, its resistance remained unchanged within the stretch of 12% strain. Then, the flexible ECG sensors has a 60dB signal-to-noise ratio, which is a prerequisite for obtaining a stable physiology signal. An ancillary signal processing circuit is designed as analog signal processing for the signal collected from the human body. Besides, digital signal processing, including analog digital converter (ADC), microprocessor, Bluetooth, and mobile application software finishes transformation, transmission, and display of the ECG signal. After usage, flexible ECG sensors can be simply delaminating within 150 seconds by smearing the deionized (DI) water on it. In conclusion, our design offers a better solution for biomedical electronics in the future.

II. RESULTS AND DISCUSSIONS

A. The Structure of the Flexible ECG Sensor

In this research, the schematic of the flexible ECG sensor is displayed in Fig. 1a. After delaminating the PVA film from the supporting PDMS substrate, a flexible ECG sensor made of the PVA film (30 ×35 ×3 mm^3) and graphene pattern (10 × 15 mm^2) is obtained (Fig. 1b.). Contact with skin schematically is showed in Fig. 1c and the whole flexible ECG sensor were anchored onto the skin with high adhesion (Table I). Because of the strong adhesion, the flexible ECG sensor keeps a strong contact with the skin when it is compressed and stretched (Fig. 1c, d). This excellent mechanical **characteristic ensures that sensor has high signal-to-noise ratio dynamically and statically**. In this research, graphene nanoplatelets are made by electrochemically exfoliated method and the schematic of the experiment is depicted in Fig. 1e.

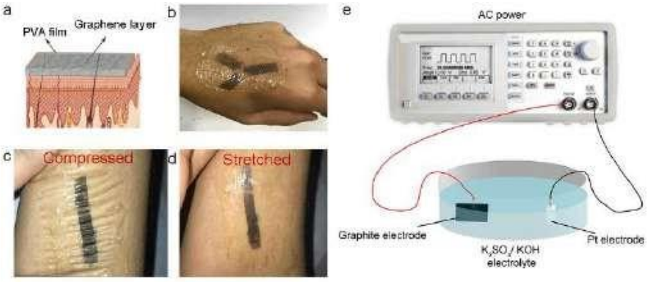

Fig. 1. The structure of the flexible ECG sensor. (a) The schematic of the flexible ECG sensor. (b) Photograph of the flexible ECG sensor on skin. (c) and (d) illustration that the flexible sensor can keep a strong contact with the skin when it is compressed (c) and stretched(d). (e) The schematic of the electrochemically exfoliated method.

TABLE I: COMPARISON OF THE DIFFERENT FLEXIBLE SENSOR

Active materials	Substrate materials	Skin conformal	Biodegradability	Ref.
Rubber dielectric layers	PDMS	No	No	9
AgNWs composite	PDMS	No	No	13
Graphene nanoparticles	PDMS	No	No	5, 14
Carbon nanotubes	PDMS	No	No	16
Graphene nanoparticles	PVA	Yes	Yes	This work

B. Mechanical Properties of Flexible ECG Sensor

Mechanical properties are crucial to wearable sensor especially the flexible sensor. Only if the flexible sensor has similar mechanical properties with human skin (20–30%) [1], it can form ultrahigh adhesion with skin. In this research, the mechanical properties of flexible ECG sensor mainly include stress-strain relationship and piezoresistive effect (Fig. 2a). The flexible ECG sensor's Young's modulus is 8.598MPa by calculating the stress-strain relationship, which is similar to that of human skin. Besides, the piezoresistive effect of the flexible ECG sensor is tested by using a motorized tension stage and a digital electric bridge. In Fig. 2b, the normalized relative resistance of the flexible ECG sensor varies almost exponentially with the stress when the strain of the flexible ECG sensor is within 135%. This piezoresistive effect of the flexible ECG sensor is due to the stretching of the graphene nanoplatelets. The stretching possessing is schematically shown in Fig. 2b, it can be concluded that the resistance would not change until there are few overlapping graphene sheets because the slip of graphene sheets would not change resistance. After almost all the overlapping sheets disappear, the resistance would change exponentially as a result of the sheets are pulled apart. According to the requirement of ECG monitor, the resistance variation of flexible ECG sensors should be as small as possible. In regard to this characteristic, the pre-stress structure is proposed to ensure the flexible ECG sensor resistance would remain unchangeable in dynamic and the manufacturing process is depicted in Fig. 2c. Besides, the photographs (Fig. 2d,e) of non-pre-stress structure and pre-stress structure using the scanning electron microscope (SEM) further confirmed the difference that there are more overlapping sheets in pre-stress structure. As mentioned above, the resistance of the pre-stress structure will not change from the lamellar dislocation (overlapping sheets) to slice alignment. And this can be confirmed by Fig. 2f, during the stretching possessing within 12%, the resistance of the pre-stress flexible ECG sensor does not change, whereas the resistance of the non-pre-stress flexible ECG sensor had changed dramatically. Besides, the gauge factor (GF= $(\Delta R/R_0)/\varepsilon$, the ΔR is the variation in resistance, the R_0 is the initial resistance and the ε is the sensor's strain), which is the sensitivity of strain sensors, retain zero within the stretch of 12% as shown in Fig. 2g. This further confirmed that the resistance of the pre-stress flexible ECG sensor does not change within the stretch of 12%. Taken together, these results combined with ultrahigh skin-conformal adhesion prove that the flexible ECG sensor is an excellent candidate for biomedical electronics.

C. Electrical Properties of Flexible ECG Sensor

In addition to mechanical properties, the electrical property of flexible ECG sensor is the prerequisite for obtaining stable signal and portable applications. Because the human physiology signal is weak(20μV–5mV) especially ECG signal, it is crucial for our system to obtain a high signal-to-noise ratio. And conformal adhesion with skin would also decrease the noise caused by friction between skin and sensor, which is the main reason for the noise. Besides, as proof of portable applications, the power consumption of the ECG measuring system is about 2mW.

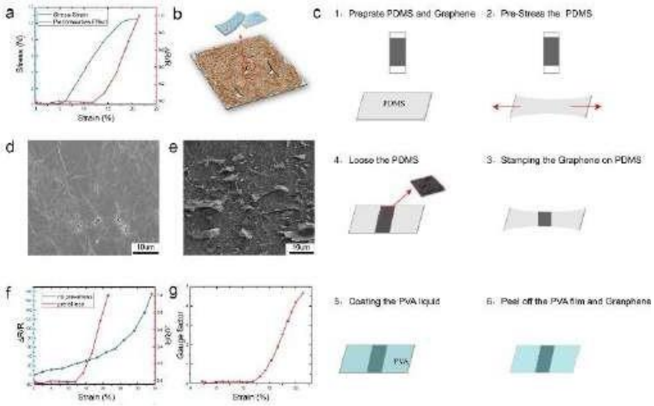

Fig. 2. Mechanical properties of flexible ECG sensor. (a) The stress-strain relationship (blue line) and piezoresistive effect (red line) of the flexible ECG sensor. (b) Schematic illustration of the stretching possessing of the flexible sensor. (c) The schematic of double transfer method. SEM image showing the surface morphology of no pre-stress structure (d) and pre-stress structure layers (e). (f) The resistance of the Pre-Stress structure (red line) and the No Pre-Stress structure (blue line) during the stretching possessing. (g) The gauge factor of the Pre-Stress structure plotted as a function of applied stress.

D. Biodegradability of the Flexible ECG Sensor

With the development of flexible sensors in recent years, handling these sensors' material after use is an important problem. Most of the flexible sensors are made from material (*e.g*. PDMS, PI *etc*.) that are non-biodegradable and this would cause environmental pollution, as well as material waste. According to the recyclable principles, the best approach is to deal with this problem by developing a biodegradable flexible sensor. The flexible ECG sensor is made of graphene and PVA and both these two materials can be disposed of by just immersing in deionized (DI) water at room temperature (~20°C). The disposing possess is demonstrated in Fig. 3a. When spraying the deionized (DI) water on the flexible ECG sensor, the sensor begins to dissolve and dramatic structural damage can be seen from the picture I to picture VI. After 150 seconds, the whole sensor is disposed without residuals. This process can prove the biodegradability of the flexible ECG sensor. Although the flexible ECG sensor can be disposed of by smeared deionized (DI) water, it is quite durable under normal conditions (temperature range of 15-30°C and humidity of 30-80%) in daily life. The resistance variation of our flexible ECG sensor is measured during the whole day, as shown in Fig. 3b. The resistance of the sensor almost remains the initial value (1.91 MΩ, the average value of ten measurements at the begin, 1.89 MΩ at the final). Besides, the sensor can remain almost the initial value after jogging for 5 minutes. Based on the characteristic above, this flexible ECG sensor can be used with stability under normal conditions and can be biodegradable after use.

E. ECG Signal Monitoring System

Taking advantage of the electrical properties and mechanical properties of our flexible ECG sensor, the ECG monitoring system is capable of real-time measurement of ECG signals. The system block diagram is schematically showed in Fig. 4a; three flexible sensors adhere simply on the left chest of the human body. The three flexible ECG sensors were connected to the ECG signal processing circuit to convert the bioelectric potential difference to the ECG signal. Then, under the control of the microprocessor, the analog signal (ECG signal) is transformed into a digital signal by ADC. Because the frequency range of the ECG signal is ranging within 1-100Hz, the transform interval time of the ADC is 1ms and counted by using the timer of the microprocessor. Next, under the control of the microprocessor, the digital signal is transmitted by the Bluetooth to the mobile terminals (mobile phone). Finally, after the processing of mobile application software, the ECG signal is displayed on mobile terminals in real-time. In conclusion, the bioelectric potential difference of humans is displayed on our cell phone by the ECG signal monitoring system. The Fig. 4b is the ECG signal displayed on the cell phone and the waves on the cell phone completely include all the characteristic waves of the ECG signal (characteristic waves include *P* wave, *QRS* wave, and *T* wave). The ECG signal displayed on the mobile phone keeps consistent with the state of human motion, the heart rate is increased while jogging and the heart rate slows down while relaxing. In order to further verify the main frequency of two states of ECG signal (relax and jogging), the FFT transform illustrate the two states of motion in Fig. 4c. Besides, the analysis of ECG signals including finding out the beginning point, the peakpoint and the end point is displayed in Fig. 4d, which can provide better guidance for the diagnosis of diseases in the future.

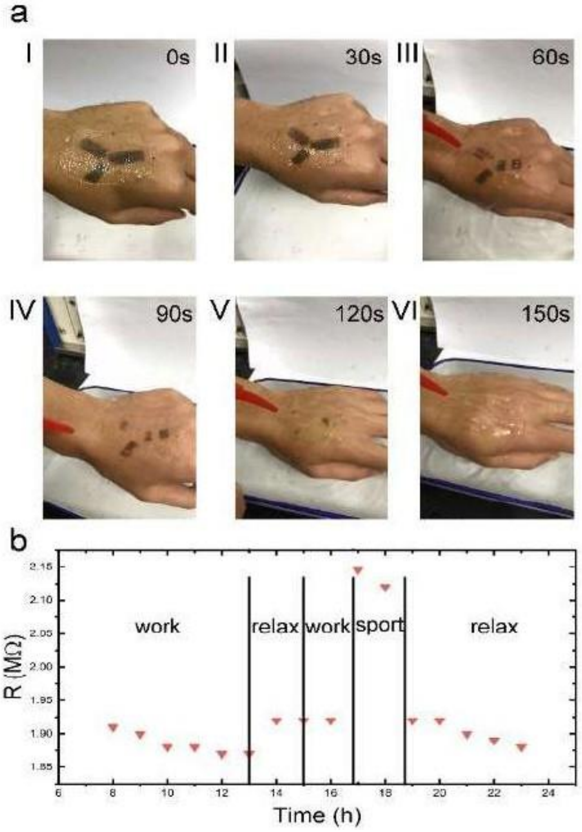

Fig. 3. Biodegradability of the flexible ECG Sensor. (a) The disposing possessing (I-VI) of the flexible sensor by spraying DI water on the sensor, the whole sensor disposed without anything after 150s. (b) The resistance variation of our flexible ECG sensor during the whole day under normal conditions.

In conclusion, the impressive performance of our flexible ECG sensor combined with miniaturized circuits and mobile terminals can achieve the measurement of the ECG signal in real-time.

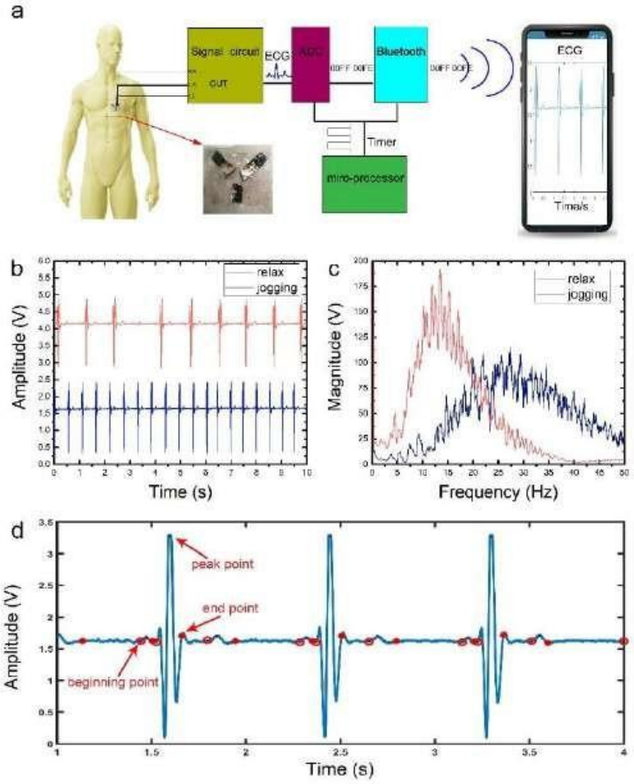

Fig. 4. ECG signal monitoring system. (a) Schematic illustration of the system block diagram including ECG signal processing circuit, ADC, the microprocessor, the Bluetooth, mobile phone. (b) ECG detected by system under different conditions such as relax (read line) and jogging (blue line). (c) FFT of ECG under different conditions, relax (read line) and jogging (blue line). (d) Analysis of ECG signals including finding out beginning point, peak point and end point.

III. CONCLUSION

Our ECG signal monitoring system comprises two kinds of components. One is an analog component included flexible ECG sensor for the detection of bioelectric potential difference signals and ECG signal processing circuit, and the other is a digital one for transformation, transmission and display of the ECG signal, including ADC, microprocessor, Bluetooth, and mobile application software. In conclusion, our work mainly focuses on the analog component, which has ultrahigh skin-conformal adhesion, high signal-to-noise ratio, and biodegradability. The combination of our flexible sensor and digital components based on silicon offers an optimized option for future wearable sensor system for biomedical electronics. By measuring human physiological signals in real time, it is efficient to obtain the state of humans and it pave the way for analyzing and discovering illness. Furthermore, stable measurement of physiological signals lays the foundation for machine learning of physiological signals in future.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

Nan Wu conducted the research and wrote the paper; Liu Hui finished the wireless system and app; Shi Su edited the whole manuscript and sorted all the references. Shu Wan managed the structure, provided constructive advice and suggestions. Litao Sun edited the whole paragraph and provided final revision. All authors had approved the final version.

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