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Carbon nanotube-based self-adhesive polymer electrodes for wireless long-term recording of electrocardiogram signals

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ABSTRACT

In this study, the concept of polymer electrodes integrated with a wireless electrocardiogram (ECG) system was described. Polymer electrodes for long-term ECG measurements were fabricated by loading high content of carbon nanotubes (CNTs) in polydimethylsiloxane. Silver nanoparticles (Ag NPs) were added to increase the flexibility of the polymer and the conductivity of the electrode. An ECG electrode patch was fabricated by integrating the electrodes with an adhesive polydimethylsiloxane (aPDMS) layer. Holes in the electrode filled with aPDMS can enable robust contact between the electrode and skin, reducing motion artifacts. A wireless ECG measurement system was developed and adapted to the polymer electrodes. The polymer electrodes combined with the measurement system were successfully applied in wireless, long-term recording of ECG signals. An eleven-day continuous test showed that the ECG signal did not degrade over time. The results of attach/detach tests demonstrated that the ECG signal was affected by motion artifacts after six attach/detach cycles. The electrodes produced are flexible and exhibit good ECG performance, and therefore can be used in wearable medical monitoring systems. The approach proposed in this study holds significant promise for commercial application in medical fields.

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Polymer electrode; carbon nanotubes; electrocardiogram; long-term monitoring

1. Introduction

Electrocardiogram (ECG) measurement is an efficient technique for recording the electrical activity of the heart in both research and clinical environments.[1] Long-term recording of ECG signals is critical for the primary diagnostic of cardiac diseases. Thus, many researchers have focused on developing wireless long-term monitoring systems for ECG measurements.[2,3]

In ECG, bio-potential signals are captured and converted to electrical signals by surface electrodes. Thus, the electrode is an essential component of the ECG signal recording system, and directly affects the quality of the resulting electrical signal. The most commonly used electrode in ECG measurements is the gel-type silver/silver chloride (Ag/AgCl) electrode.[4] An electrolyte gel is used to establish electrical contact between the skin and electrode, thus

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ensuring good signal quality. However, the gels in such electrodes can cause skin irritation and allergies, and the drying of the gel over time significantly decreases the signal quality. This limits the use of gelled electrodes in wearable applications and long-term monitoring.[5] Dry electrodes have been proposed to overcome these problems.[6] Polymer-based flexible electrodes have received much attention as dry electrodes, because they are comfortable to wear and are suitable for long-term monitoring.[7,8]

A simple method to convert a polymer to a conductive material is through loading it with conductive fillers.[9–11] Carbon nanotubes (CNTs) are the most compatible conductive fillers in polymers, because they are tangled and assembled randomly, imparting excellent contact within the polymer matrix. The addition of CNTs increases the polymer conductivity but can also reduce the polymer flexibility, especially when present at high density. Embedding nanoparticles into an elastic polymer matrix can improve the stretchability of such electrodes.[12,13] In our study, silver nanoparticles (Ag NP) were added to the polymer to counter the stiffness caused by the addition of CNTs at high content. Polydimethysiloxane (PDMS) was chosen as the base polymer material because it is flexible, nontoxic, biocompatible and easy to fabricate.[14] Although the percolation threshold of CNT-PDMS is 4%, the proper range of the filler content is suggested to range approximately from 8 to 18 wt%.[15]

The degree of CNT dispersion in PDMS directly influences the electrical properties of the composite electrode but it is difficult to achieve thorough-mixing of CNT and PDMS to obtain good conductivity, especially with high CNT content. Lu et al. fabricated high-density CNTs-PDMS composite materials (CNT concentration: 4–25 wt%) with a chloroform-dilution method.[15] However, chloroform is toxic and therefore is not suitable for fabricating ECG electrodes. In our study, ethanol was used as the solvent and a similar dilution process was adopted to obtain conductive polymers with a high-content of CNTs. A simple and efficient dispersion method was described in our previous study.[16] Here, that method was adopted, with modifications to enable a high CNT density.

CNT-based PDMS electrodes are already used for the recording of ECG signals.[11,17] However, most of these electrodes are fabricated to include a snap fitting for convenient connection to the measurement system. The snap fitting increases the thickness of the electrode, which may affect the robustness of contact between the electrode and the skin when body postures are changed. Furthermore, these electrodes are not self-adhesive requiring other tools such as tapes to attach to the skin. In our study, Cu wires were embedded in the electrode as a connector between the electrode and printed circuit board, which significantly decreased the thickness of the electrode. Adhesive PDMS (aPDMS), which has good biocompatibility and mechanical properties,[2] was used to affix the electrode to the skin. The electrodes were integrated with aPDMS in the ECG electrode patch. To accomplish robust contact between electrode and skin, several holes were punched in the electrode and filled with aPDMS to aid firm attachment to the skin. A wireless ECG measurement system was designed to obtain high-quality signals. Wireless transmission was achieved through a radio-frequency (RF) module. The properties of the polymer electrode were evaluated by impedance and ECG measurements. Long-term recording of ECG signals were also carried out to evaluate the performance of the whole system.

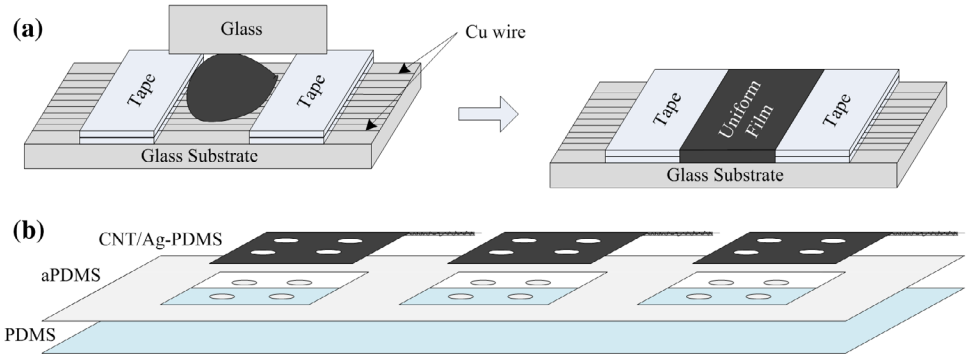

Figure 1. (a) schematic of the fabrication process of CNT/Ag-PDMS electrode; (b) structure of the ECG electrode patch composed of a PDMS base, an aPDMS layer and the polymer electrodes.

2. Materials and methods

2.1. Materials

Multi wall CNTs (>95%) of length 50 μm and Ag NPs (>99%) of diameter 80–90 nm were purchased from XFNANO Material Technology Co., Ltd., Nanjing, P. R. China. PDMS monomer (Sylgard® 184B), a curing agent (Sylgard® 184A) and adhesive polydimethylsiloxane (aPDMS, MG7-9850)were supplied by Dow Corning (China) Holding Co., Ltd., Shanghai, P. R. China. Absolute ethanol and methanol (AR grade) were purchased from Sigma-Aldrich Co. LLC. (St. Louis, U.S.A.).

2.2. Electrode fabrication

The conductive polymer mixture was fabricated following the method described in our previous study,[16] with modifications. In brief, CNT and Ag NP, both at 11 wt% were ultrasonically dispersed in ethanol; PDMS monomer was added to the suspension and magnetically stirred for 2 h; the mixture was heated on a hot plate to remove most of the ethanol while stirring with a mechanical stirrer; and the mixture was further processed in an oven to remove the remaining solvent. The modification to the previous method was the addition of the heat-stirring process to prevent particle agglomeration at high density. Finally, a curing agent was added at a ratio of PDMS monomer: curing agent = 10:1. The mixture was stirred with a glass rod, to prepare a homogeneous CNT/Ag-PDMS mixture. The ultrasonication time, during which the CNT and Ag NP in ethanol were placed in a bath sonicator, was set to 4–14 h with the interval of 2 h. Six groups of mixtures with different ultrasonication time were prepared to evaluate the influence of ultrasonication time on the conductivity of the final polymer electrode.

The polymer electrode was fabricated using the Doctor Blade Technique.[18] The fabrication process is shown in Figure 1(a). Two tapes, with the thickness of 0.2 mm, were attached to the glass in parallel. Several parallel Cu wires with a diameter of 50 μm were wound on top of the tapes and used to link the sheet electrode to the system circuitry. Two tapes were pasted onto the first-layer tapes to fix the wires. The CNT/Ag-PDMS mixture was coated between the tapes and then the surface was scraped with a glass plate. Subsequently, the

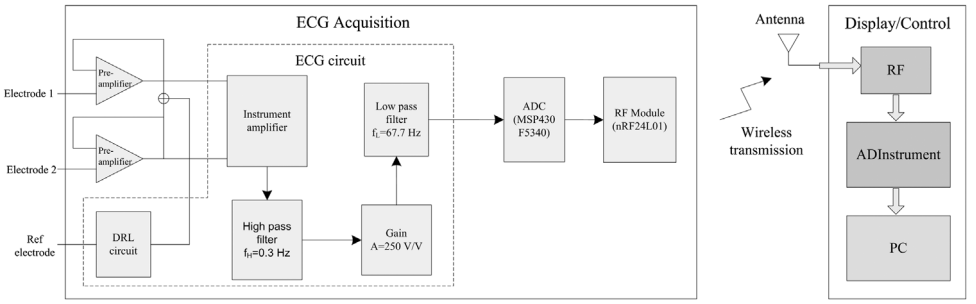

Figure 2. Schematic for wireless ECG measurement system.

sheet was thermally cured at 100 °C for 4 h and finally detached from the glass surface to obtain a flexible sheet, incorporating wires. The wires were then twisted into a bundle and the sheet was cut into 20 × 20 mm pad containing four holes, 4 mm in diameter. To fabricate electrodes with different thickness, more tapes can be pasted onto the second-layer tapes. In this study, two kinds of electrodes with thickness of 0.4 and 0.6 mm were fabricated.

2.3. Three-electrode patch

The ECG recording system applied was a three-electrode configuration. To conveniently and directly attach the electrodes to the skin, aPDMS was introduced. The fabrication process used to integrate the three polymer electrodes with adhesive pads was as follows: PDMS was poured onto a rectangular glass plate (square: 100 × 50 mm) and cured at 70 °C in an oven. The three electrodes were placed on the top of the PDMS layer in a row, separated by 10 mm gaps. aPDMS was then coated on top of the PDMS layer at the location where the electrodes were uncovered, including the holes in the electrodes. The entire structure was cured at 70 °C in an oven and then the three-electrode patch was peeled off the glass base. Cu wires were threaded into the back of the electrode patch and connected to the measurement circuit. The structure of the electrode patch is shown in Figure 1(b). The thickness of the aPDMS layer was slightly lower than that of the electrodes to guarantee a tight contact between the electrode and the skin.

2.4. ECG measurement system

To achieve wireless recording of ECG signals, the measurement system consisted of an ECG acquisition module and a display/control module. The wireless transmission was achieved through an RF module and an antenna between the two components. The ECG acquisition component consisted of two preamplifiers, an ECG circuit, an analog to digital converter (ADC) and an RF module. Figure 2 shows a schematic of the ECG measurement system. As shown in Figure 2, the signals from the two preamplifiers were differentiated by an instrument amplifier (INA118, Texas Instruments), and then high-pass filtered (f_H = 0.3 Hz) to eliminate offsets and fluctuations. The output signal was further amplified with a gain of 250 to improve the signal-to-noise ratio. A low-pass filter with a 67.7 Hz cutoff frequency was used to reduce external noise such as that due to power lines. The driven-right-leg (DRL) electrode method was adopted to minimize the common-mode interference of the subjects.

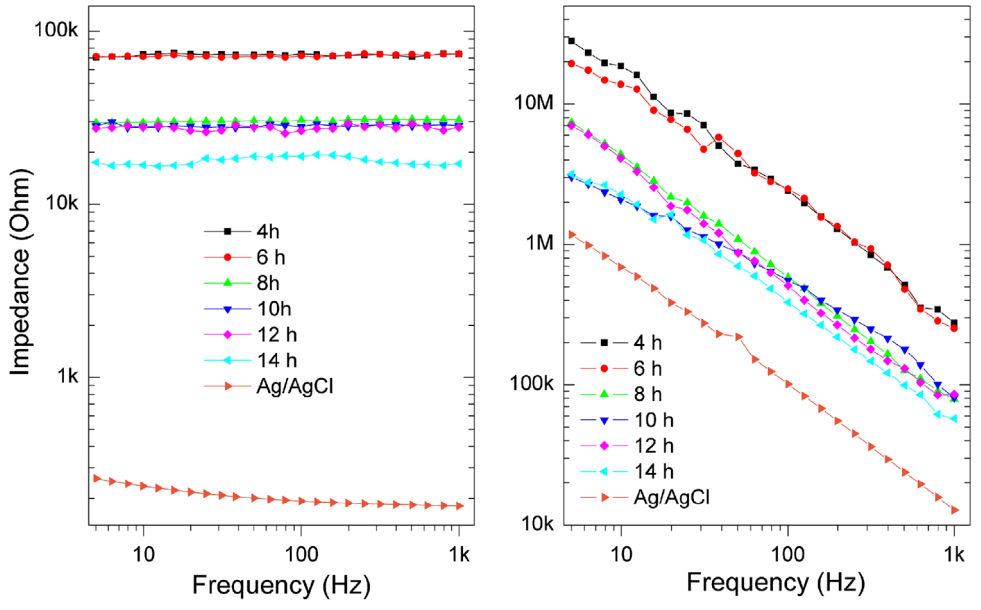

Figure 3. (a) impedance and (b) contact impedance between electrode and skin from 5 to 1 kHz at different ultrasonication time.

[19] The signal coming from the ECG circuit was digitized at a sampling rate of 1 kHz by a microcontroller (MSP430F5340, Texas Instruments), and then was transmitted to display/control end through a RF module (nRF24L01, Nordic Semiconductor). Finally, ECG data were captured using an AD Instruments acquisition system and LabChart software (AD Instruments Co., Dunedin, New Zealand).

3. Results and discussion

3.1. Impedance measurements

The electrical properties of the polymer electrode were evaluated by impedance measurements. The electrode and electrode-skin contact impedance were measured by an EIS module of a ZAHNER Im6ex instrument (ZAHNER-Elektrik GmbH & Co. Kronach, Germany). The data were achieved from 5 Hz to 1 kHz under 10 mV AC. For electrode-skin contact impedance measurements, two electrodes were fixed on the forearm without skin preparation. The polymer electrodes were of the same dimensions (20 × 20 × 0.6 mm). The impedance of polymer electrodes under different ultrasonication times was measured and for comparison, the impedance of Ag/AgCl electrodes was also measured under the same conditions. Five sets of polymer electrodes were tested and the moderate curves are shown in Figure 3. The standard deviation of the five measurements is 5.1 KΩ for electrode impedance and 6.7 MΩ for contact impedance, respectively.

The impedance of the polymer electrodes was resistive and almost constant at all frequencies, as shown in Figure 3(a). The impedance values at 4–14 h ranged from 10 to 80 kΩ. Compared with the contact impedance, a change in the intrinsic impedance will not significantly affect the performance of the electrode. Figure 3(b) shows the contact

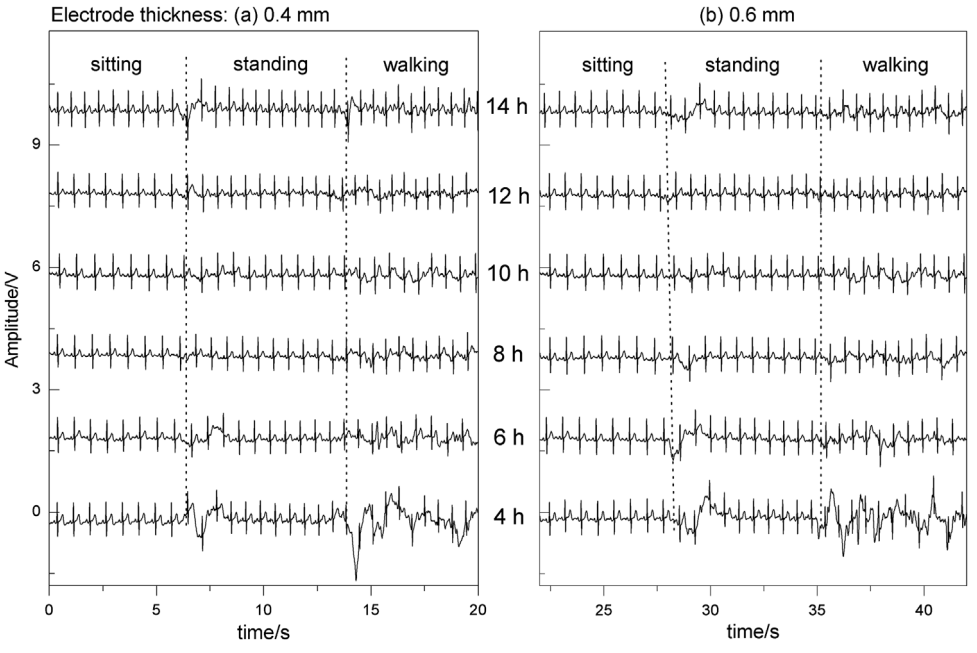

Figure 4. ECG measurements. Electrode thickness: (a) 0.4 mm; (b) 0.6 mm.
Note. The dash lines show the signal changing when body posture was altered.

impedance spectrum as a function of frequency at different ultrasonication time. The contact impedance decreased as the frequency increased from 5 Hz to 1 kHz. This decrease occurred because the capacitive component largely contributed to the total impedance at high frequency. The impedance values of the electrodes at 4 and 6 h were larger than those of the electrodes at 8–14 h. We therefore conclude that the CNTs require a percolation time to achieve homogenous dispersion in the solvent, which consequently affects their dispersion in the polymer matrix. The impedance of the Ag/AgCl electrodes was lower than that of the polymer electrodes because of the existence of the gel between the Ag/AgCl electrode and skin.

3.2. ECG measurements

For ECG measurements, the three-electrode patch was attached to the chest. Five subjects were tested using the polymer electrodes (age: 20–40; 3 male, 2 female). For different subjects, the signal amplitude varied. However, the trend of the signal changing was similar. The data shown in the study was measured with a female of 30. Figure 4 shows ECG measurements under different ultrasonication time used during preparation and different electrode thickness. With wireless transmission, the subject could freely move around the house during the ECG measurements.

The results show the continuous recording of ECG signals during three different body postures (sitting-standing-walking). When the subject was sitting or standing steadily, the baseline was flat and the signal was stable. While walking, the baseline floated up or down and motion artifacts became evident. The signals also changed when body posture was

altered. The signals differed under different ultrasonication time. At 4 and 6 h, the ECG signals jumped when posture was changed and motion artifacts were large during walking. At 8 and 10 h, motion artifacts and signal changes were reduced. At 12 h, the signal reached a stable stage. While at 14 h, the signal quality started to decline. Although the impedance measurements (Figure 3) show a lower value with the electrodes at 14 h, the motion artifacts are higher than that with the electrodes at 12 h. Lu et al. confirmed that ultrasonication of CNTs for a long time resulted in the generation of defects on CNT surface.[20] Extended ultrasonication would destroy the CNT structure and deteriorate both the electrical and mechanical properties of the CNT-polymer composites.[21,22] From the results, better signal quality could be achieved under the ultrasonication time of 12 h. There is no need to further increase the ultrasonication time.

These results demonstrate that signal changes caused by transferring postures were more obvious with electrodes prepared at ultrasonication time 4–6 h than those prepared at 8–14 h. The signals got from the electrodes under ultrasonication time of 4–6 h were more easily affected by motion due to the higher contact impedance of these electrodes. No marked differences were observed between the ECG signals from electrodes prepared at ultrasonication time 8–12 h. The signals were relatively steady and no large jump in signals occurred when postures were changed.

With different electrode thickness, a slight increase in signal amplitude was observed when the electrodes were 0.6 mm thick (see Figure 4(b)). The trend in signal changes was consistent with one another between the two-dimensional electrodes.

When compared with our previous study,[16] 11 wt% CNT was applied to achieve stable conductive polymers and avoid difficulties in electrode fabrication associated with the introduction of too high a content of CNT. The presented electrodes were fabricated with embedded wires and either 0.4 or 0.6 mm thick, which largely decreased the thickness of the electrodes fabricated with metal snaps (2 mm in thickness) in our previous study.[16] Different from our previous study, ambulatory ECGs could be measured with the measurement system integrated into the electrode patch.

Compared with other CNT-PDMS electrodes,[11,17] the polymer electrodes fabricated in this study had a high density, which guarantee stable electrode conductivity. By loading Ag NP in the polymer, the flexibility of the composite was increased and the conductivity was somehow strengthened. Compared with the methods referred to the microfabrication technique,[7] the polymer electrode fabrication method presented here was straightforward and easier to accomplish. It does not require expensive instruments and can be widely applied in conventional laboratories. The electrode patch is self-adhesive and does not need extra materials to affix it to the skin. The holes in the electrode help to achieve robust contact between the electrodes and skin, thus reducing motion artifacts. The ECG measurement system can be integrated into the electrode patch and the whole system can be further miniaturized in the future.

3.3. Long term ECG measurements

Long-term ECG measurements were accomplished with a three-electrode patch prepared under an ultrasonication time of 12 h and an electrode thickness of 0.6 mm. The electrode patch was attached to the chest and the comparison of ECG signals achieved with Ag/AgCl electrodes and CNT/Ag-PDMS electrodes at stationary state is shown in Figure 5(a). The

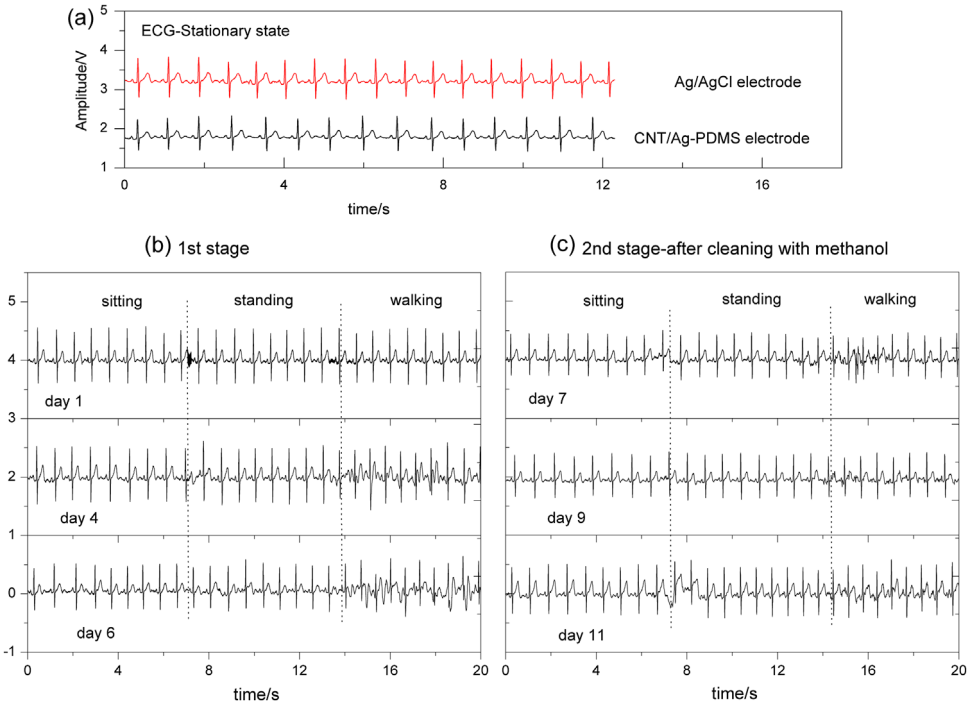

Figure 5. (a) ECG signals at the stationary state with the Ag/AgCl and polymer electrodes; long-term continuous recording of ECG signals: (b) 1–6 days; (c) 7–11 days.
Note. The dash lines show the signal changing when body posture was altered.

signal amplitude with the polymer electrodes was lower than that of the Ag/AgCl electrodes. The average amplitude of *R*-wave is 0.89, 0.98 V for the polymer and Ag/AgCl electrodes, respectively. This is consistent with the conductivity of these two kinds of electrodes.

Long-term recording and the detach/attach testing were also carried out, wherein the patch was detached and re-attached to the chest after each day. That is, the first day was also the 1st time of attachment. ECG signals were measured every day and no significant variations were observed in the first 5 days. However, after five detach/attach cycles, the adhesion force was not strong enough for skin attachment. The signal floated significantly during walking on day 6 (the 6th attachment) because the adhesion force was too low to achieve robust contact between the electrode and skin, such that motion artifacts became evident. Figure 5(b) shows the first stage of the ECG signal recording. The adhesive force of the sheet can be largely recovered by cleaning it with methanol. Figure 5(c) shows the ECG signals after the cleaning procedure. The same as shown in the first stage, in the first 4 days after cleaning (days 7–10), the ECG signals were stable and motion artifacts were small. On day 11 (the 5th attachment after cleaning), motion artifacts were again obvious and the signal jumped when posture changed.

These results show that the ECG signal strength did not degrade over time. The electrical properties of the polymer electrode were stable and very suitable for the long-term recording of biosignals. The attachment force of the adhesive layer decreased as the number of detach/attach cycles increased and would be unsatisfactory after six cycles. The adhesive layer is merely a medium to help the electrode attach to the skin and can be replaced by

new materials. We expect that this can be improved in the future. There is no apparent red or itchy feeling on the skin after eleven days of wearing, which indicates that the polymer electrode is suitable for long-term wearability.

4. Conclusions

A high-density CNT-PDMS mixture was fabricated using a simple and efficient dispersion method. Ag NPs were added to the mixture to improve the flexibility of the electrode. The polymer electrodes were fabricated by the Doctor Blade Technique. A self-adhesive ECG electrode patch was fabricated by integrating three electrodes with an aPDMS layer which is used to attach to the skin. Several holes were punched in the electrode and filled with aPDMS to achieve a robust contact between the electrodes and skin. An ECG acquisition system was designed and combined with an RF module to accomplish the wireless long-term recording of ECG signals. The properties of the polymer electrodes were evaluated by impedance and ECG measurements. An eleven-day continuous recording of ECG signals was carried out to evaluate the performance of the whole system. The signal amplitude did not degrade over time and no allergy was evident on the skin, indicating that the polymer electrode is suitable for use in long-term monitoring. The electrode fabrication method is straightforward and suitable for mass production. The presented polymer electrodes will be applied in long-term healthcare systems after being statistically tested.

Disclosure statement

No potential conflict of interest was reported by the authors.

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