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Silver nanowire-composite electrodes for long-term electrocardiogram measurements

Benyan Liu [a,b], Zhangyuan Luo [a,b,*], Wenzan Zhang [a,b], Quan Tu [a,b], Xun Jin [a,b]

[a] Ensense Biomedical Technologies (Shanghai) Co., Ltd., 201112 Shanghai, China
[b] Genix Biotek Technologies (Shanghai) Co., Ltd., 201112 Shanghai, China

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ABSTRACT

Composite electrodes are fabricated for long-term electrocardiogram (ECG) measurements. The electrode consists of a polydimethylsiloxane base, silver nanowire layer, and adhesive layer. The adhesive layer is fabricated by loading carbon nanotubes into adhesive polydimethylsiloxane. An electrode patch consisting of three composite electrodes and an adhesive polydimethylsiloxane layer is fabricated and combined with a wireless acquisition system to obtain ECG measurements. The composite electrode patch is self-adhesive and can conform to the skin, achieving robust contact between electrode and skin and thus decreasing motion artifacts. The composite electrodes combined with the measurement system are successfully used for wireless long-term recording of ECG signals. Continuous testing for 8 days shows that the ECG signal amplitude decreases slightly after wearing for 6 days and can be largely recovered by cleaning with ethanol. The composite electrodes are flexible and exhibit good ECG performance, and therefore can be used in wearable medical monitoring systems.

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1. Introduction

Long-term electrocardiogram (ECG) monitoring can provide a wealth of information that is helpful for the early diagnosis of cardiac diseases [1,2]. ECG biosignals are usually recorded through surface electrodes. Conventional silver/silver chloride (Ag/AgCl) electrodes use an electrolytic gel layer to enhance the clarity of biopotential recordings. However, the gel dries over time causing signal degradation, and can irritate the skin. Therefore, although Ag/AgCl electrodes give high-quality signals, they are not suitable for long-term monitoring [3]. Polymer electrodes are considered as an alternative to Ag/AgCl electrodes for use in long-term ECG monitoring [4].

Polymer electrodes are endowed with conductivity by coating with a metal layer [5,6] or loading with a conductive filler [7–10]. Metal-coated polymer electrodes can display excellent conductivity and thus provide good ECG signal quality. Using such electrodes, the metal layer is in direct contact with the skin and additional equipment such as a tape or a belt is required to fix the electrode to the skin. In addition, the fabrication of metal-coated polymer electrodes requires costly instruments and extra processing to prevent the metal layer delaminating from the flexible polymer [11]. In contrast, the method used to fabricate polymer composite electrodes loaded with conductive fillers is simple and does not require expensive equipment. However, the conductivity of such electrodes is lower than that of metal-coated polymer electrodes (the conductivity of the metal-coated electrode in Ref. [5] is about 107 S/m; while that of the composite electrode in Ref. [7] is 9×10^{-2} S/m). The lower conductivity results in decreased amplitude of the signal, and further decreased the signal to noise ratio, which limits ECG signal quality. Furthermore, most such electrodes also require other materials to adhere to skin.

In this study, composite electrodes are fabricated by both coating a conductive layer on a polymer surface and loading conductive fillers into a polymer matrix. To realize robust contact between the electrode and skin, adhesive polydimethylsiloxane (aPDMS), which has good biocompatibility and mechanical property [12,13], is used as a medium to achieve a conductive adhesion layer. Carbon nanotubes (CNTs) are the most compatible fillers for polymer composites to achieve conductivity [14]. We obtain well-dispersed CNT–aPDMS mixtures using a simple dispersion method [15].

To simplify the fabrication process of the metal-coated polymer electrode, silver nanowires (Ag NWs) are used as an alternative to a conductive metal layer. Ag NWs are press-printed onto the surface of a polymer to generate a highly conductive surface [16]. The composite electrodes are attached to wireless ECG measurement system designed to carry out long-term monitoring.

* Corresponding author at: Ensense Biomedical Technologies (Shanghai) Co., Ltd., 201112 Shanghai, China.
E-mail address: zyluo@esnmed.com (Z. Luo).

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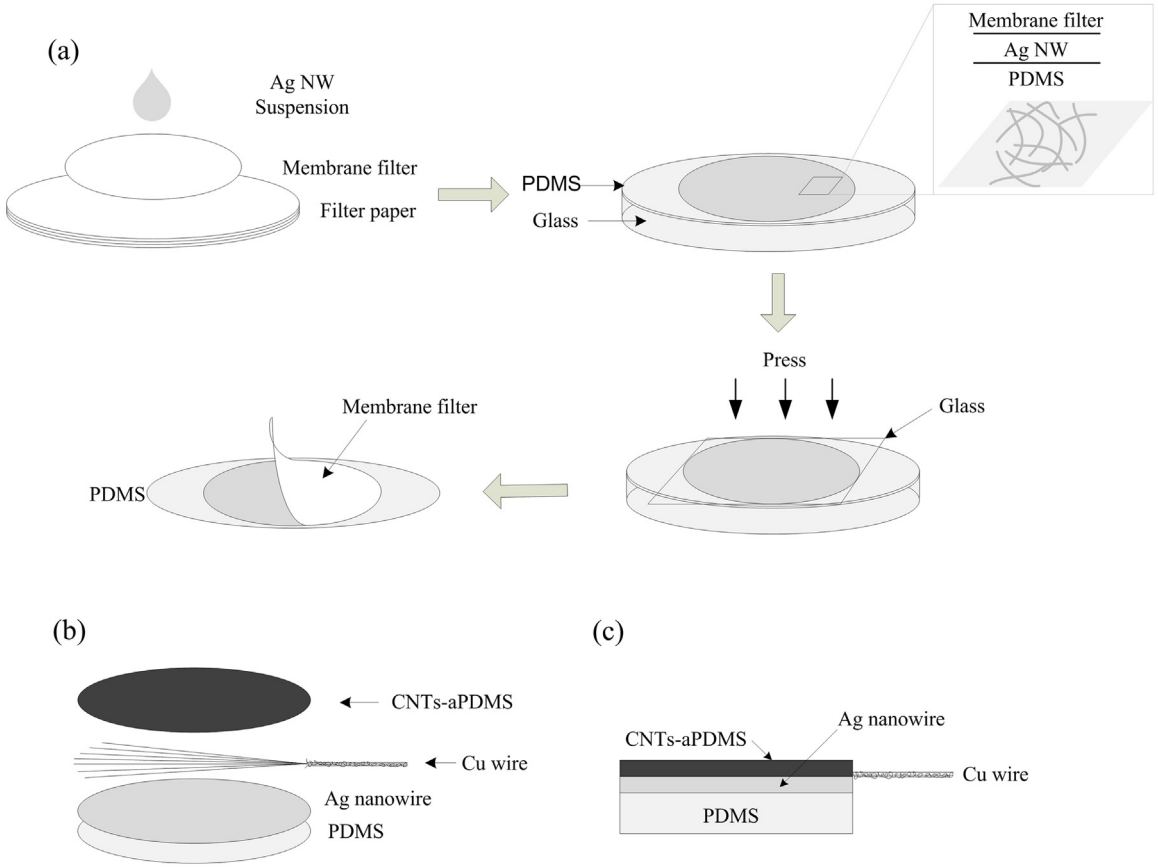

Fig. 1. (a) Schematic of the fabrication process of Ag NW layer on PDMS; (b) structure of the composite electrode composed of a PDMS base, Ag NW layer, Cu wires and CNT-aPDMS layer; (c) a side view of the composite electrode.

2. Experimental

2.1. Materials

Multi wall CNTs (>95%) of length 50 μm and Ag NWs (diameter: 120 nm, length: 20 μm) were purchased from XFNANO Material Technology Co., Ltd., Nanjing, P. R. China. PDMS monomer (Sylgard® 184B), a curing agent (Sylgard® 184A) and aPDMS(MG7-9850, two components: A and B) were supplied by Dow Corning (China) Holding Co., Ltd., Shanghai, P. R. China. Absolute ethanol (AR grade) was purchased from Sigma-Aldrich Co. LLC. (St. Louis, USA). The mixed cellulose ester membrane filter (diameter: 25 mm, a pore size of 0.22 μm in diameter) was purchased from Taoyuan Medical Chemical Instrument Factory, Haining, P. R. China.

2.2. Composite electrode fabrication

The composite electrode consisted of a PDMS base, Ag NW layer, CNT–aPDMS layer and embedded Cu wires to connect with the external circuitry. The Ag NW layer was fabricated as shown in Fig. 1(a). First, PDMS was poured on a glass plate and cured at 70 °C for 10 min to form a support layer. Ag NW and ethanol (C: 1 mg/mL) were mixed ultrasonically for 30 min using a bath sonicator (40 kHz, 80 W; JP-010B; Jiemeng Cleaning Equipment Co., Ltd, Shenzhen, P.R. China). The Ag NW suspension was added dropwise onto a filter membrane (diameter: 25 mm) and dried to give Ag NWs coated on the surface of the membrane. After drying, the membrane was turned over and placed on the PDMS layer pressed with a glass plate to transfer the Ag NWs to the PDMS surface. The whole structure was cured at 70 °C for 30 min. The membrane was peeled off, leaving the Ag NWs on the surface of the PDMS layer. The margin of PDMS without Ag NWs was cut off to give a round PDMS layer coated with an Ag NW layer.

A CNT–aPDMS mixture was fabricated following the method used in our previous study [12] with modifications. CNTs (3 wt%) were ultrasonically dispersed in ethanol. Then the A component of aPDMS was added to the suspension, and it was magnetically stirred for 2 h. The mixture was heated on a hot plate to remove most of the ethanol while being stirred with a mechanical stirrer, and then heated in an oven at 100 °C for 24 h to remove the remaining solvent. The B component of aPDMS was added with a ratio of aPDMS A: aPDMS B = 0.8. The usual ratio of aPDMS A: B for solidification is 1; the ratio was adjusted here because of the presence of CNTs. The mixture was stirred with a glass rod to prepare a homogeneous CNT–aPDMS mixture.

Cu wire with a diameter of 50 μm was wound on top of the Ag NW layer and then the top of the Ag NW layer was coated with the CNT–aPDMS mixture, embedding the wires in the electrode. The whole structure was cured at 100 °C for 2 h. The wires were then twisted into a bundle to allow convenient connection with the circuitry. The structure of the electrode is depicted in Fig. 1(b).

2.3. ECG electrode patch and measurement system

The ECG recording system used the three electrode configuration. Three electrodes were integrated into an ECG electrode patch as follows. PDMS was poured onto a glass plate (100 × 50 mm) and cured at 70 °C for 30 min in an oven. A thin layer of aPDMS with an A: B ratio of 1 was poured on top of the PDMS substrate. Three electrodes were carefully placed on top of the aPDMS layer in a row

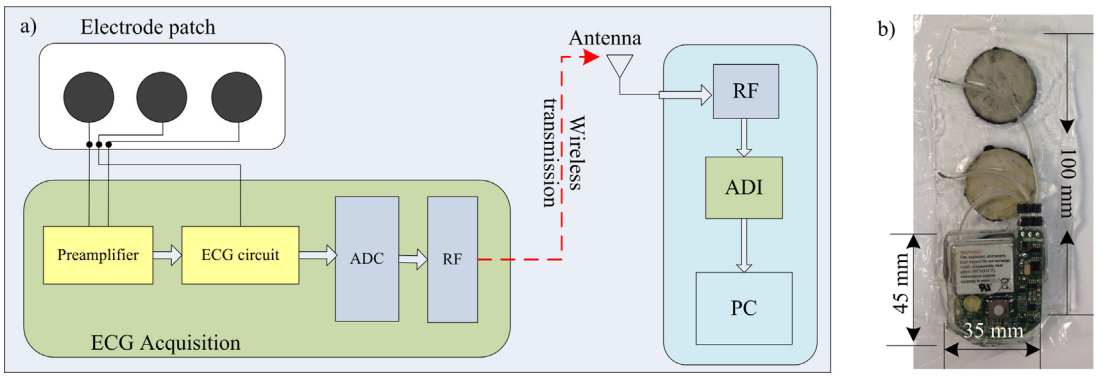

Fig. 2. (a) Schematic of the electrode patch combined with the measurement system. (b) A photo image of the electrode patch with the circuit system.

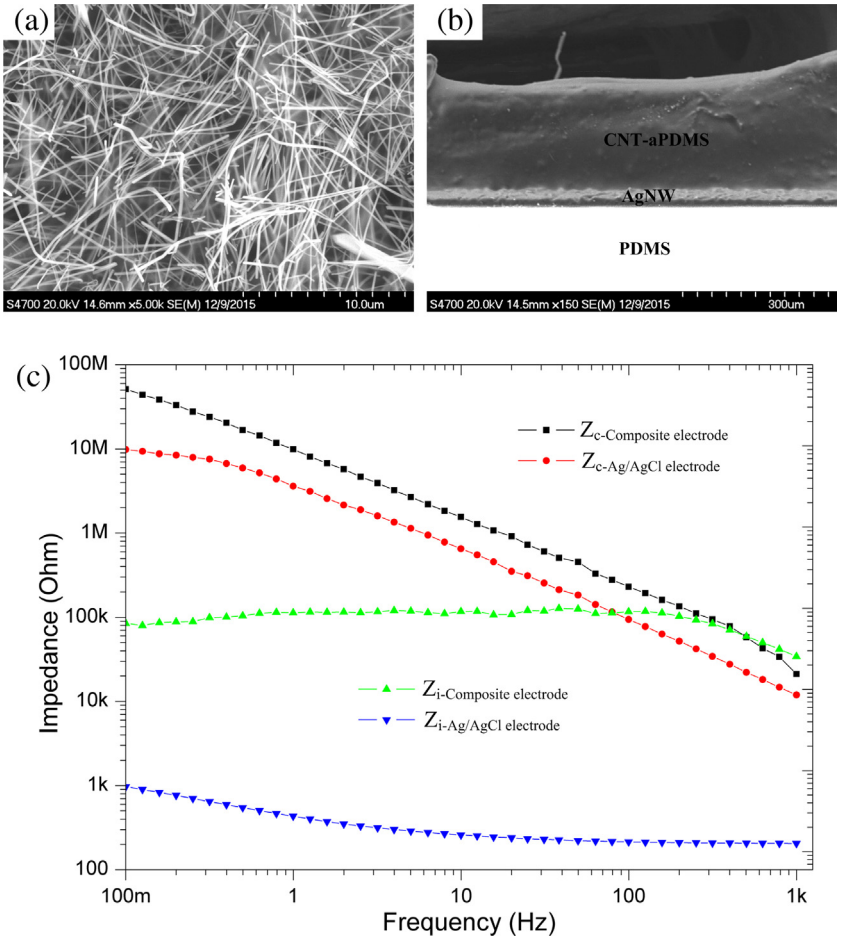

Fig. 3. (a) SEM image of a network of randomly distributed AgNWs. (b) SEM image of the three-layer structure of composite electrode. (c) Comparison of impedance and contact impedance between electrode and skin measured with the composite and Ag/AgCl electrodes from 0.1 Hz to 1 kHz. Z_i: intrinsic impedance of electrode; Z_c: electrode-skin contact impedance.

separated by 10-mm gaps. The whole 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 Fig. 2a.

An ECG measurement system containing the composite electrodes was designed. As illustrated in Fig. 2a, wireless transmission was achieved through a radio-frequency (RF) module. The ECG measurement circuit consisted of a preamplifier, ECG circuit, analog-to-digital converter and RF module. The data from the preamplifier passed to an instrument amplifier (INA118, TI) and were high-pass filtered (f_H = 0.3 Hz), amplified (gain: 250) and low-pass filtered (f_L = 67.7 Hz) to eliminate noise and improve the signal-to-noise ratio. The ECG circuit contains a driven-right-leg circuit to minimize the common-mode interference of the subjects [17,18]. The signal coming from the ECG circuit was digitized and sampled at 1 kHz by a microcontroller (MSP430F5340, TI), and then transmitted wirelessly via the RF module (nRF24L01, Nordic Semiconductor, Oslo, Norway). Finally, ECG data were captured using an AD Instruments acquisition system and LabChart software (AD Instruments Co., Dunedin, New Zealand).

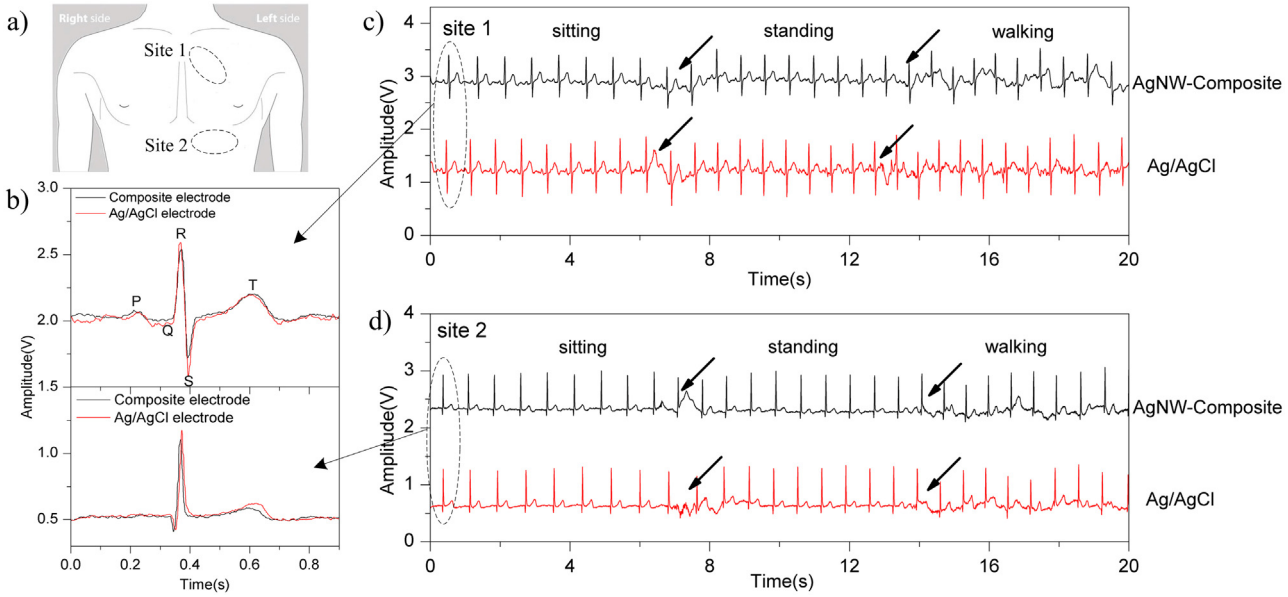

Fig. 4. ECG measurements. (a) The measurement sites. (b) ECG signal comparison of the waves between the composite and Ag/AgCl electrodes. The continuous recording of ECG signals when different postures were altered at (c) site 1 and (d) site 2. The arrows in (c) and (d) show the signal changing when the subject changed his body posture.

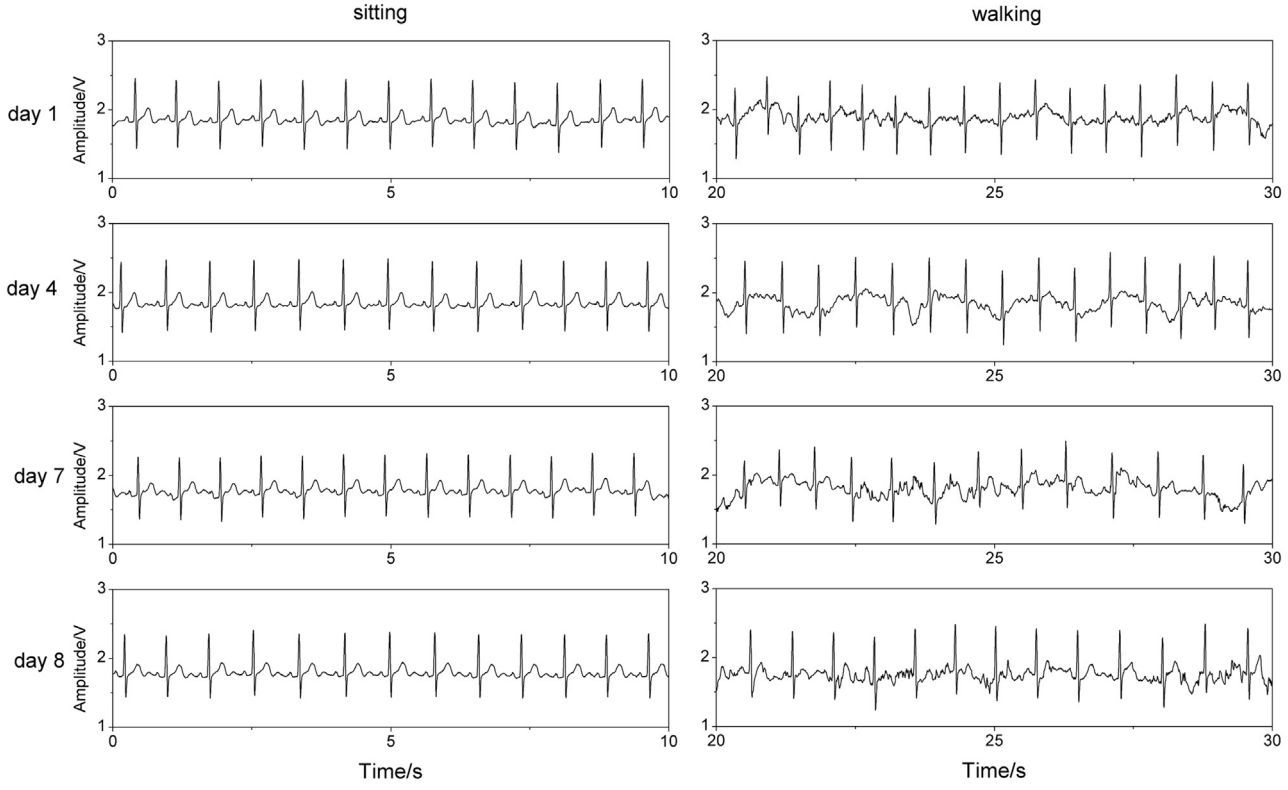

Fig. 5. Long-term ECG measurements. ECG waveforms measured during sitting and walking for day 1, 4, 7, and day 8 after cleaning.

The picture of the circuit and electrode patch is shown in Fig. 2b. The bottom of the circuit was coated with aPDMS and can be attached to the electrode patch and also can be pasted on the skin.

2.4. 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 impedance analyzer (Im6ex, Zahner-Elektrik GmbH & Co. Kronach, Germany). Data were measured from 0.1 to 1 kHz under an AC voltage of 10 mV. For the intrinsic impedance measurements, two electrodes were put together face to face and the connectors of the electrodes were linked to the analyzer. To obtain electrode–skin contact impedance measurements, two electrodes were fixed on the forearm without skin preparation.

3. Results and discussion

3.1. Electrode structure and impedance

Scanning electron microscope (SEM) images of the Ag NW layer and composite electrode are provided in Fig. 3. The Ag NWs are randomly oriented on the PDMS surface. Cross-sectional views of the electrode structure are shown in Figs. 1 (c) and 3 (b). The three-layer structure is clearly observed in the SEM image. The Ag NW and CNT–aPDMS layers were approximately 20 and 200–μm thick, respectively.

The intrinsic and contact impedances of the composite and reference Ag/AgCl electrodes are presented in Fig. 3c. The impedance of the composite electrode is much higher than that of the Ag/AgCl electrode. This is because of the low conductivity of the CNT–aPDMS layer. The contact impedance of the composite electrode is approximately 1.55 MΩ at 10 Hz, while that of the Ag/AgCl electrode is 651 kΩ.

3.2. ECG measurements

The ECG waveform of the electrode patch was compared with that of the reference Ag/AgCl electrode. Fig. 4 shows the results at different sites for the composite and Ag/AgCl electrodes, and the measurement sites are displayed in Fig. 4(a). At site 1, each wave of the ECG signal (P, QRS complex, and T) can be clearly recognized, as shown in Fig. 4(b). At site 2, the P wave, which indicates the activity of atrial depolarization, was not distinguished because the electrode patch was fixed close to the ventricle so the waveforms mainly record the activity of the ventricle. The signal amplitude of the Ag/AgCl electrodes was larger than that of the composite electrodes. The average amplitude of the R–wave for the composite electrode at site 2 was 0.708 V, while that of the Ag/AgCl electrode was 0.74 V. This is consistent with the larger contact impedance of the composite electrode than that of the Ag/AgCl electrode.

The ECG waveforms presented in Fig. 4c and d show the continuous recording of signals during three different postures (sitting, standing, and walking). The signals were noiseless and stable during sitting and standing. The stable flat baseline measured while sitting and standing shows that the composite electrode is well attached to the skin. The effect of motion on signal quality was investigated by taking ECG measurements as body posture changed and when the subject was walking. The signal was affected by the change of posture. While walking, the waveforms obtained using both of the composite and Ag/AgCl electrodes displayed a considerable amount of noise and wandering baseline. The signal changes observed for the Ag/AgCl and composite electrodes were similar, indicating that the composite electrode performed as well as the commercial Ag/AgCl electrode.

The composite electrode is flexible and stretchable, and can conform to the curvilinear surfaces of the body. This lowers skin–electrode impedance and eliminates most motion artifacts. When compared with other composite electrodes [7,8], the electrode fabricated in this study is self-adhesive, and robust contact with skin is achieved without other tools (glue or tape), which decreases motion artifacts. Furthermore, the electrode contains an Ag NW layer that has high conductivity, guaranteeing the quality of ECG signals. Compared with electrodes fabricated by a microfabrication technique [5,6,13], the fabrication method presented here is simple and does not require expensive instruments.

3.3. Long–term ECG measurements

Long–term ECG measurements were accomplished using a three–electrode patch attached to site 1. The ECG signals measured over 8 days are provided in Fig. 5. ECG signals were measured every day and the waveforms show the signals of two states (sitting and walking).

The signals obtained during sitting were noiseless and almost identical. During walking, baseline noise became evident. No significant variations of ECG signals were observed over the first 5 days. On day 7, the ECG signal amplitude was slightly decreased compared with those of the previous 6 days. This was because the robust contact between electrode and skin weakened after 6 days. During wearing, skin secretions like perspiration and sebum acted on the electrode, decreasing the adhesive force of the CNT–aPDMS layer. On day 8, the adhesion force of the CNT–aPDMS layer was largely restored after cleaning with ethanol, which reinforced the contact between the electrode and skin and partly recovered the signal strength. The average values of the R-wave on day 1, 7, and 8 were 0.97, 0.89, and 0.94, respectively.

These results indicate that the electrode can be used several times because the adhesion force can be largely recovered by cleaning. After wearing for 8 days, no allergic reaction was observed at the wearing site, which indicates that the composite electrode is suitable for long-term wear. This is because the Ag NW layer was sandwiched between PDMS and CNT–aPDMS layers, avoiding the action of metal on skin and also retaining the conductivity of the electrode.

4. Conclusions

A polymer composite electrode composed of a PDMS substrate, Ag NW layer, CNT–aPDMS layer and Cu wires was fabricated for ECG measurements. The electrode was flexible and self-adhesive, realizing conformal contact between electrode and skin. An electrode patch was fabricated with three composite electrodes and an aPDMS layer, which strengthened the robust contact between the electrodes and skin. The electrode patch combined with a wireless measurement system was successfully used for long-term ECG measurements. The composite electrode patch performed as well as Ag/AgCl electrodes. The electrode can be reused several times because its adhesion force can be recovered by cleaning. The electrode did not cause reactions on skin, indicating it is suitable for long-term ECG monitoring.

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Biographies

Benyan Liu received the B.S. degree in electronic science and technology from Shandong University, Shandong, China, in 2006, and the Ph.D. degree in Microelectronics & Solid electronics from Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai, China, in 2012. She is currently in the Department of Research and Development, Ensense Biomedical Technologies (Shanghai) Co., Ltd. Her current research interests focus on flexible biomedical electrodes and microfabrication.

Zhangyuan Luo received the B.S. degree in Biomedical Engineering from Shanghai University of Science and Technology, Shanghai, China, in 2008, and the M.S. degree in Software Engineering from Dalian University of Technology, Dalian, China, in 2012. He is currently Electronics Engineer and R&D Manager of Ensense Biomedical Technologies (Shanghai) Co., Ltd. His current interests include intelligent micro-medical system and instrument development; Systematic design of wearable biomedical instrument and novel medical ECG electrodes.

Wenzan Zhang received the B.S. degree in biomedical engineering from Shanghai Jiao Tong University, Shanghai, China, in 1992. He is currently the founder and CTO of Ensense Biomedical Technologies (Shanghai) Co., Ltd. His current interests lie in ultra-low power electronic circuit and system design for implantable and wearable biomedical devices.

Quan Tu received the B.S. degree in mechanical engineering from Beijing Union University, Beijing, China, in 1990, and the M.S. degree in biomedical engineering from Huazhong University of Science and Technology, Wuhan, China, in 1997. He is currently the co-founder of Ensense Biomedical Technologies (Shanghai) Co., Ltd. His current interests include biomedical digital signal processing and pattern recognition.

Xun Jin received the B.S. and M.S. degress in biomedical engineering from Tsinghua University, Beijing, China, in 2004 and 2008 respectively. He is currently Electronic Engineer and Technical Director in Ensense Biomedical Technologies (Shanghai) Co., Ltd. His current interests lie in ultra-low power electronic circuit and system design for implantable and wearable biomedical devices.