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SHORT COMMUNICATION

A novel method of fabricating carbon nanotubes-polydimethylsiloxane composite electrodes for electrocardiography

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Polymer-based flexible electrodes are receiving much attention in medical applications due to their good wearing comfort. The current fabrication methods of such electrodes are not widely applied. In this study, polydimethylsiloxane (PDMS) and conductive additives of carbon nanotubes (CNTs) were employed to fabricate composite electrodes for electrocardiography (ECG). A three-step dispersion process consisting of ultrasonication, stirring, and *in situ* polymerization was developed to yield homogenous CNTs–PDMS mixtures. The CNTs–PDMS mixtures were used to fabricate CNTs–PDMS composite electrodes by replica technology. The influence of ultrasonication time and CNT concentration on polymer electrode performance was evaluated by impedance and ECG measurements. The signal amplitude of the electrodes prepared using an ultrasonication time of 12 h and CNT content of 5 wt% was comparable to that of commercial Ag/AgCl electrodes. The polymer electrodes were easily fabricated by conventional manufacturing techniques, indicating a potential advantage of reduced cost for mass production.

Keywords: polydimethylsiloxane; carbon nanotubes; composite electrode; dispersion; electrocardiography

1. Introduction

Polymer-based electrodes have attracted an increasing interest in the application of long-term medical monitoring systems.[1] Such electrodes have good wearing comfort and are considered as an alternative to the commercial silver/silver chloride (Ag/AgCl) electrodes, which are not suitable for long-term monitoring owing to the degradation of signal quality with time and skin allergy reactions.[2]

Polymer-based electrodes are generally fabricated by a conductive coating on polymer surfaces,[3,4] or achieved by polymer composites.[5,6] Conductive coating is usually accomplished by microfabrication technology, which requires precisely controlled environments and experimental conditions.[4] In contrast, polymer composites, consisting of additives and polymer matrices, can be easily fabricated by conventional manufacturing techniques, a potential advantage of reduced cost for mass production of nanocomposites.[7] This method was used in the current study, to ensure that the electrode fabrication process could be widely applied.

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Polydimethylsiloxane (PDMS) has been widely used in biomedical applications, because of its flexibility, nontoxicity, biocompatibility, high gas permeability, and ease of fabrication.[8] Mixing PDMS with conductive additives can yield a conductive polymer. Among the conductive materials, carbon nanotubes (CNTs) are the most compatible additives with polymeric materials. CNTs are tangled and assembled randomly, which allows them to have a better contact with each other in a polymer matrix. Thus, the conductive polymers can be achieved at a low content of CNTs. Moreover, CNTs are inexpensive and highly accessible.[9]

Fabricating CNTs–PDMS composites requires the dispersion of CNTs within PDMS. The dispersion degree of the CNTs in PDMS is a critical factor that affects the properties of the polymer composites. The most common method is stirring, which was applied by Prajith et al. [6] to achieve a homogenous mixture for composite electrode fabrication. However, the performance of the electrodes was not as good as the commercial Ag/AgCl electrodes. The dispersion of CNTs in a polymer matrix can be improved by tuning the dispersion method. Jung et al. employed a three-roll milling machine not widely available to optimize the dispersion process.[10]

In our study, a three-step dispersion process involving ultrasonication, stirring, and *in situ* polymerization [11] was used to disperse untreated CNTs in PDMS. CNTs–PDMS composite electrodes were fabricated using varying ultrasonication time and CNT concentrations. The influence of ultrasonication time and CNT content on electrode performance was evaluated by impedance and electrocardiographic (ECG) measurements.

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2. Materials and methods

2.1. Materials

Multi-wall CNTs (>95%) of length 50 μm were purchased from XFNANO Material Technology Co., Ltd, Nanjing, P.R. China. PDMS monomer (Sylgard® 184B) and a curing agent (Sylgard® 184A) 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).

2.2. Dispersion of CNTs in PDMS

Ultrasonication is an effective method to disperse CNTs in low-viscosity liquids. PDMS used in this study is in a viscous liquid state. The homogeneous mixture of CNTs and PDMS cannot be achieved by direct ultrasonication. So, CNTs were treated with a liquid solvent before mixing with PDMS. Stirring is a common technique to disperse particles in liquid systems and can be used to disperse CNTs in a polymer matrix.[6,10] *In situ* polymerization can uniformly disperse CNTs in thermosetting polymers.[11] These methods were combined in the current study to achieve a homogenous dispersion of CNTs in PDMS. The dispersion process was separated into three steps: CNTs were firstly ultrasonically dispersed in a solvent; then the CNT suspension was mixed with PDMS monomer and re-dispersed by stirring; at last, a curing agent was added to realize *in situ* polymerization. The dispersion process is shown in Figure 1(A). Specifically, CNTs were dispersed in ethanol using a water bath sonicator (40 kHz, 200 W; JP-040s; Jiemeng Cleaning Equipment Co., Ltd, Shenzhen, P.R. China). PDMS monomer was then added to the CNT suspension. Subsequently, the mixture was stirred for 2 h at

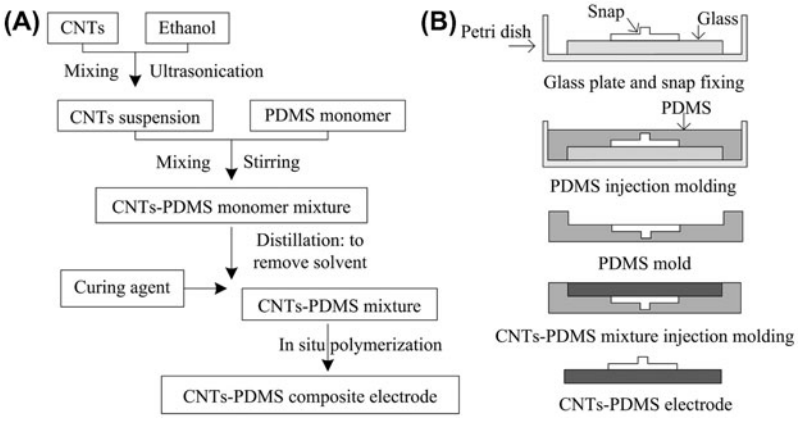

Figure 1. (A) Schematics of dispersion process and fabrication of CNTs–PDMS composite electrodes; (B) summary of fabrication process of CNTs–PDMS composite electrodes.

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300 rpm using a magnetic stirrer. This caused the CNTs to become incorporated into the PDMS monomer. PDMS is insoluble in ethanol; therefore most ethanol could then be poured out. The mixture was placed in an oven at 100 °C for 36 h to remove the remaining solvent, yielding a mixture of CNTs–PDMS monomer. At last, the curing agent was added at a PDMS monomer: curing agent ratio of 10:1. The mixture was stirred with a glass rod, to prepare a homogeneous CNTs–PDMS mixture.

2.3. *Fabrication of CNTs–PDMS composite electrodes*

CNTs–PDMS composite electrodes were fabricated as shown in Figure 1(B). The first step involved the fabrication of a PDMS mold. A round glass plate (diameter: 20 mm and thickness: 2 mm) was placed in the center of a Petri dish (diameter: 35 mm). A steel snap for connecting to the signal acquisition system was placed on top of the glass plate. Then, a mixture of PDMS monomer and curing agent with a ratio of 10:1 was degassed to remove any bubbles, and poured over the snap. The resulting Petri dish and its contents were cured at 75 °C for 1 h in an oven. After curing, the PDMS with steel snap was carefully separated from the Petri dish, yielding the PDMS mold. The second step involved fabricating the CNTs–PDMS composite electrode using replica technology.[12] The prepared CNTs–PDMS mixture was poured into the PDMS mold, which was then placed in a vacuum dryer to remove the air bubbles. The mixture was then cured at 100 °C for 1 h, after which the CNTs–PDMS composite electrode was peeled away from the mold.

3. Results and discussion

3.1. *Impedance measurements*

The electrical properties of the CNTs–PDMS composite electrode were evaluated by measuring the electrode impedance and electrode-skin contact impedance. The impedance was measured using an EIS module of ZAHNER Im6ex (ZAHNER-Elektrik GmbH & Co. Kronach, Germany). The data were measured at 1 Hz under 10 mV AC.

For electrode-skin contact impedance measurements, two electrodes were fixed on the forearm using a compression bandage without skin preparation. The electrodes were at the same dimension (diameter: 20 mm and thickness: 2 mm).

The ultrasonication time affects the dispersion degree of CNTs in ethanol, which affects its subsequent dispersion in PDMS. Impedance was measured as a function of ultrasonication time, as shown in Figure 2(A). The impedance of the electrode decreased as the ultrasonication time increased from 10 to 12 h. The impedance only slightly changed between 12 and 16 h, indicating that impedance was saturated with respect to ultrasonication time during this period. When the ultrasonication time continued to increase, the impedance increased correspondingly. In case of the electrode-skin contact impedance, the value decreased as the ultrasonication time increased from 10 to 14 h. The contact impedance at 16 h was similar to that at 14 h. The contact impedance increased as the ultrasonication time continued to increase to 20 h. Thus, the electrode impedance and contact impedance exhibited similar trends with ultrasonication time.

The CNT content in PDMS affected the electrical property of the composite electrode. The impedance at different CNT concentrations is shown in Figure 2(B). The impedance decreased with increasing CNT concentration from 4 to 6 wt%. The electrode-skin impedance exhibited a similar trend. The increasing CNT content resulted in a lower impedance, which indicated better conductivity (DC conductivity = 1/(surface resistance [Ω/sq] × thickness [m])).[10] However, the CNTs–PDMS mixture became more viscous when the CNT content was >6 wt%, making the electrode fabrication process more difficult. In addition, high CNT content may decrease the flexibility of PDMS.

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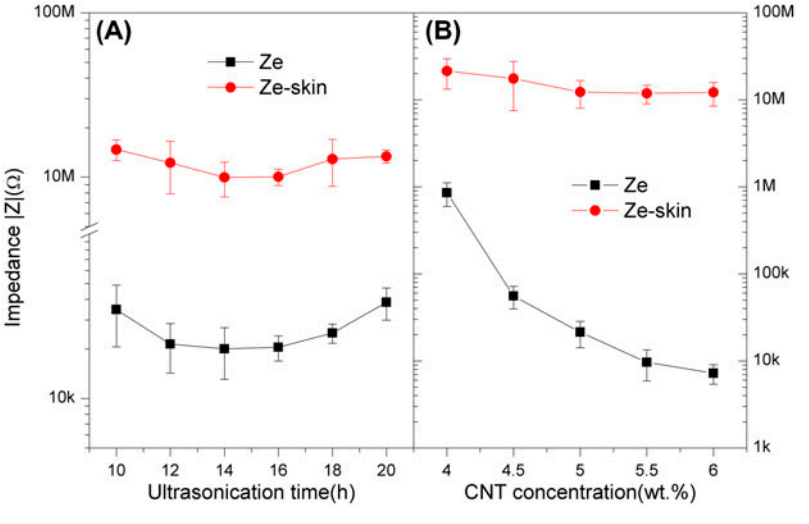

Figure 2. Influences of ultrasonication time (A) and CNT concentration (B) on electrode (Z_e) and electrode-skin contact impedance (Z_{e-skin}). Conditions: (A) CNT concentration: 5wt%; (B) ultrasonication time: 12 h (impedance values are the mean of five measurements).

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3.2. ECG measurements

ECG measurements were carried out using an AD Instruments acquisition system and LabChart software (AD Instruments Co., Dunedin, New Zealand). Electrodes were placed on the forearms and right leg. The dimension of composite electrodes was with a diameter of 20 mm and a thickness of 2 mm. The ECG signals were successfully achieved using the CNTs–PDMS composite electrodes. For comparison, the signals from commercial Ag/AgCl electrodes (3 M Co., Chicago, USA) were measured under the same conditions. The influence of ultrasonication time and CNT content on ECG signals was evaluated, and the results are shown in Figure 3.

The ECG signals were affected by the CNT content (Figure 3(B)) and ultrasonication time (Figure 3(C)). The ECG signal amplitude increased as the CNT content increased, displaying a similar trend with the impedance. The ECG signal amplitude increased slightly, as the ultrasonication time increased from 10 to 16 h. The signal amplitude decreased when the ultrasonication time was further increased to 20 h. This was probably because extended ultrasonication destroyed the CNT structure, weakening the bonding between the CNTs and PDMS, which reduced the conductivity of the composite electrode. This resulted in the reduction of signal quality.

As shown in these results, the ECG characteristics components, which include the *P* wave, QRS complex, and the *T* wave, were clearly distinguished. The optimum ECG signal was achieved after ultrasonication for 16 h (the signal amplitude of *R* wave was 0.374 mV; signal-to-noise ratio was 31.2 dB). There is no significant difference in terms of signal amplitude between the ECG signals obtained with the Ag/AgCl electrodes and CNTs–PDMS electrodes prepared by ultrasonication for 12 h and containing 5 wt% CNTs. The average values of *R*-wave amplitude for these two type electrodes were

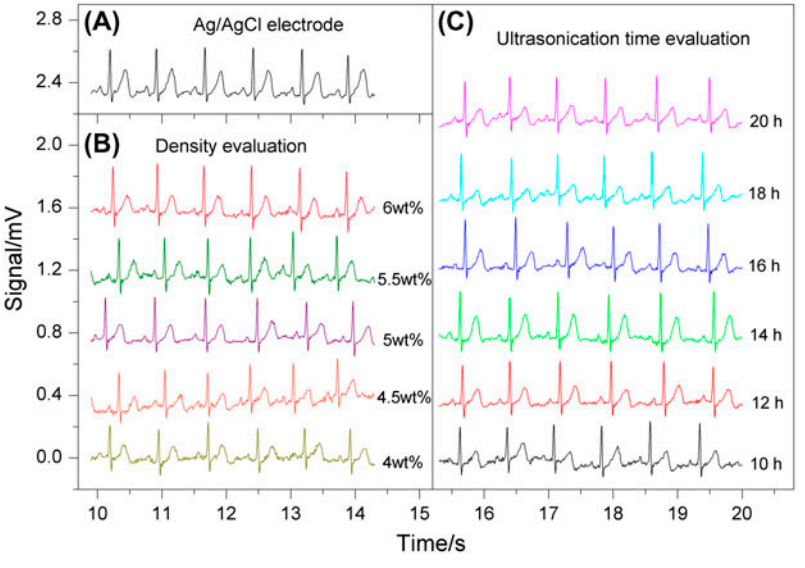

Figure 3. ECG signals of different electrodes. (A) commercial Ag/AgCl electrode; (B) 5 types of CNTs–PDMS composite electrodes with different CNT contents and (C) 6 types of CNTs–PDMS composite electrodes with different ultrasonication times. Conditions: ultrasonication time for (B) was 12 h; CNT content for (C) was 5 wt%.

0.337 and 0.341, respectively. The signals of electrodes prepared by ultrasonication for 14 and 16 h were even better, indicating that the CNTs–PDMS composite electrodes performed well in ECG measurements.

The presented method to disperse CNTs into PDMS and fabricate CNTs–PDMS composite electrodes was straightforward. It did not require rigid experimental conditions or expensive instruments and can be widely applied in conventional laboratories. Prajith et al. [6] reported a method employing mechanical stirring to disperse CNTs into PDMS. The method was simple, but the electrode was large (diameter: 40 mm) and the performance of the composite electrode was not sufficiently confirmed. When comparing with the method reported by Jung et al. [10], which employed a three-roll milling machine to achieve homogenous mixtures, the method used in our study is easier to accomplish and the signal quality of the composite electrode was satisfactory.

4. Conclusions

A novel dispersion method of incorporating CNTs into a PDMS matrix was developed to achieve a homogenous CNTs–PDMS mixture. CNTs–PDMS composite electrodes were fabricated by replica technology. Dispersion and fabrication did not require expensive instrumentation. The properties of the CNTs–PDMS composite electrodes were evaluated by impedance and ECG measurements. The signal amplitude of the electrodes (ultrasonication time: 12 h and CNT content: 5 wt%) was comparable to that of conventional Ag/AgCl electrodes. The fabrication method of the polymer-based electrode is based on the conventional manufacturing techniques and suitable for mass production. Flexible CNTs–PDMS composite electrodes have potential in wearable medical monitoring systems.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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