Ionic Liquid Regenerated Cellulose Membrane Electroless Plated By Silver Layer For ECG Signal Monitoring

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Abstract

Flexible electrodes have attracted the interest of a wide range of people because they can monitor human health signals like ECG, EMG and EEG as wearable devices. However, PDMS-based membrane electrodes have the problem of difficulty in depositing metal layers, while fabric electrodes have high contact impedance. Furthermore, the widely used Ag/AgCl electrodes have the shortcomings of skin inflammation or skin irritation. Therefore, we fabricate a skin-like electrical conductive electrode via electroless silver plating on the surface of regenerated cellulose membrane, in which the cellulose membrane is obtained by the dissolution of cotton fiber with green solvent ionic liquid [Bmim]Cl. The as-prepared biocompatible electrode with low skin-electrode contact impedance can be used as a dry electrode for a long-term period of use. The impedance at 700 Hz is only 8 k Ω /cm², and the conductivity can reach 252 S/cm. After 5 hours of wear, the skin contact impedance of the electrode was only 10 k Ω /cm² under 700 Hz (when AgNO₃ was used at a concentration of 0.20 mol/L). Importantly, the electrodes not only provide a stable and clear ECG signal, but also offer a high level of comfort and low impedance, when used for long-term health monitoring.

Introduction

With the increasing attention paid for the health of current society, the electrocardiograph (ECG), electromyogram (EMG) and electroencephalogram (EEG) sensors have been widely used in personal healthcare and hospital medical devices to monitor human heart activity (Faezipour and Faezipour 2020; Lam et al. 2020; Shimauchi et al. 2021; Tan et al. 2011; Yoon et al. 2009). The electrodes can be divided into wet and dry electrodes according to whether electrolytes are used or not. The conventional commercial wet electrode is Ag/AgCl electrode, but it has the problem of the conductive gel dries out with time, so it is not suitable for long-term use. Therefore the concept of dry electrodes was proposed. Most of the current dry electrodes are built on fabric, such as cotton fabric, polyester fabric, conductive silk is woven fabric, they are too heavy, which will reduce the comfort of the user (Nigusse et al. 2020a; Wang et al. 2021a; Xu et al. 2019; Yun et al. 2014). And there is a gap between the contact interface of fabric electrodes and skin, which will increase the contact impedance of the acquisition interface, thus leading to poor quality of the acquired ECG (Beckmann et al. 2010; Catrysse et al. 2004). Therefore, in order to improve the quality of ECG signal monitoring, it is imperative to develop flexible electrodes that can be in common contact with the skin.

To reduce the skin-electrode contact impedance of electrodes, many scholars have reported electrodes based on polydimethylsiloxane (PDMS), polyethylene terephthalate (PET) and polyimide (PI). For example, Nishat T et al. (Tasneem et al. 2020) were prepared MWCNT/PDMS composite polymer which is integrated with the Kapton substrate to fabricate the flexible, biocompatible and low skin-electrode impedance electrodes. Kwang-Seok Kim et al. (Kim et al. 2018) were prepared stretchable transparent electrodes by using pulsed light (IPL) to induce plasma heating that irradiated AgNWs which deposited on cured TPU films. Junshan Liu et al. (Liu et al. 2020) fabricated a flexible and stretchable three-layer dry electrode by transfer printing method, which excellent conformability, stretchability, low electrode-skin

contact impedance. Although they have numerous advantages, they are all polar materials with high viscosity, which makes it difficult to disperse MWCNTs in PDMS, and in addition, when they are combined with metals, they are poorly compatible with each other, which can lead to the failure of stable bonding of metal layers.

There are many methods of depositing metals on substrates, such as electroless plating, coating, magnetron sputtering, etc. Electroless plating in essence is a redox chemical reaction of metal ions, which is deposited onto the surface of the substrate by reducing the metal ions to monomers using a reducing agent. Mojtaba Sarafpour et al. (Sarafpour et al. 2017) have coated polypropylene fabrics with copper particles by using electroless plating, screen printing, and arc spraying processes. The tensile strength, electrical conductivity, air permeability, thermal conductivity and fog collection capacity of electroless plated copper on fabrics were higher than those of screen printed and sprayed copper-coated fabrics. Magnetron sputtering, also known as plasma plating, mainly involves the deposition of atoms from the target material onto the substrate by using ions with high energy impacting on the target material. Ronghui Wu et al. (Wu et al. 2019) fabricated a flexible wearable pressure sensor by magnetron sputtering prepared from conductive nylon fabric as an electrode and elastomer Ecoflex as a dielectric layer. The coating method was used to prepare conductive fabrics by applying coatings containing conductive fillers (e.g., metal powders) to fabrics. Abreha Bayrau Nigusse (Nigusse et al. 2020b) coated silver ink onto cotton and polyester fabrics by screen printing for ECG signal monitoring. However, after coating, the substrates are always stiff and cannot comfortably attach on the human body or joints. And magnetron sputtering is limited its use because of its high price. Therefore, it is particularly important to develop biocompatible electrodes with low electrode skin contact impedance in an expedient and environmentally friendly way.

Cellulose is abundant on the earth and is an environmentally friendly material. Cellulose and its derivatives have been widely used as raw materials for membrane production in plastics, filtration and food (Mu et al. 2019; Wang et al. 2015; Wetterling et al. 2017). There are many dissolution systems for cellulose, including N-methyl morpholine-N-oxide (NMMO), alkaline aqueous dissolution systems, ionic liquids and LiCl/DMAc(N,N-di-methylacetamide)etc. NMMO can dissolve cellulose directly (Zhao et al. 2007). However, it has problems such as higher prices, harsh dissolution conditions and harder to control reaction by-products etc (Rosenau and French 2021). LiCl/DMAc does not lead to any thermal runaway reaction, moreover, in the LiCl/DMAc process, no additives or special equipment are needed and it can be recycled, but LiCl is expensive (Huber et al. 2011). In contrast, as a kind of green solvent, ionic liquids are not only recyclable, but also do not pollute the environment; they have high thermal and chemical stability. Bomou Ma et al (Ma et al. 2016). prepared cellulose membranes by using [Bmim]Cl, which has good thermal stability and high moisture regain. In addition, cellulose membranes are highly biocompatible and flexible, making them good flexible base materials.

Herein, an electrical conductive electrode with low skin contact impedance is fabricated by electroless silver plating on a regenerated cellulose film (RCM). Preparation of RCM by dissolving cotton fibers in ionic liquids is an environmentally friendly and no require of excessive reagents. In addition, electroless

plated is a simple and effective method for metal deposition. The resultant electrode was characterized by FTIR, thermogravimetry, field emission scanning electron microscopy, XRD. Furthermore, the electrochemical properties and relative ECG monitoring properties tests were also conducted.

Experimental Section

2.1 Materials

In this experiment, the Cotton fabric was commercially available from Shanghai San yuan Co. Ltd., [Bmim]Cl was supplied by Shanghai Bidder Medical Technology Co. Ltd., polyethylene glycol, glucose, potassium sodium tartrate, palladium chloride, ethanol and ethylenediamine were obtained from Sinopharm Chemical Reagent Co. Ltd., ammonia was received from Beijing Yinuo Technology Co., Ltd., potassium hydroxide was acquired from Shanghai Lingfeng Chemical Reagent Co. Ltd., silver nitrate was purchased from Shanghai Titan Technology Co. Ltd.

2.2 Preparation of RCM

RCM was prepared by using [Bmim]Cl. Add 4.0 g of ionic liquid to the round bottom flask under 110 °C oil bath to melt to transparent yellow, then add 0.2 g of cotton fiber to the flask mechanical stirring until completely dissolved with cotton fiber (when no cotton fibers could be observed with a microscope). After complete dissolution, the solution was allowed to stand in a flask at 110°C for 30 min to de-bubble, poured into the mold, added to the solution with water as the coagulation bath to dissolve the regenerated cellulose hydrogel, soaked in the aqueous solution for 24 hours to completely remove [Bmim]Cl to obtain the regenerated cellulose hydrogel, and finally dried naturally to obtain the transparent RCM.

2.3 Preparation of Ag-RCM

Ag-RCM was prepared by electroless plating. Firstly, to prepare the reducing solution, 2 g of glucose, 0.125 g of potassium sodium tartrate and 0.003 g of polyethylene glycol were weighed and dissolved in 50mL of distilled water, then 2 mL of ethanol was added and shaken to make it mixed well. Second, prepare silver ammonia solution, weigh AgNO_3 dissolved in 12.5 mL distilled water, add ammonia dropwise until the solution just changed from turbid to clarified, then add the prepared 0.3g KOH dissolved in 2.5 mL distilled water solution to get dark brown solution, add ammonia dropwise to make it clarified, add 2 mL ethylenediamine and shake well. Thirdly, the cellulose membrane was put into the reducing solution, and then the silver ammonia solution was poured into the reducing solution and sonicated at 40°C for 55 minutes. Finally, the Ag ions on the surface were removed and rinsed with deionized water to obtain Ag-RCM.

2.4 Characterization

Fourier infrared spectroscopy

The infrared spectral profiles of Cellulose and RCM were obtained with a Fourier infrared spectrometer (FTIR, Nicolet 6700, USA) at frequencies of 500-4000 cm⁻¹.

Thermogravimetric analyzer

Thermal stability curves of cellulose, RCM, Ag-RCM were obtained with a thermogravimetric analyzer under nitrogen atmosphere at 0-900 °C with a heating rate of 10 °C/min.

Field emission scanning electron microscopy

The morphology of cellulose and Ag-RCM were characterized by field emission scanning electron microscopy.

18KW rotary target X-ray diffractometer (D/max-2550VB+/PC)(XRD)

The structure of the thin silver layer on the cellulose film substrate was analyzed by using an 18 KW rotary target X-ray diffractometer (D/max-2550VB+/PC).

Conductivity testing

Electrical properties were measured using a four-point probe setup (RTS-8). The conductive film is chemically stable and can be tested directly for conductivity according to equation (1).

$$\delta = 1/R_s * d \quad (1)$$

Among Eq. 1, R_s is the sheet resistance of the film and d is the thickness of the film.

Electrical performance evaluation

The impedance, EIS, and open-circuit voltage performance of the electrodes were tested using an electrochemical analyzer (CHI 660E, Chen Hua, China). Impedance EIS measurements were performed in the frequency range of 0.01 Hz to 100kHz. The open-circuit voltage sweep has a tracing time of 30 s, a sampling interval of 0.1s, and a high potential of 1 V and a low potential of -1 V.

Electrode stability tests

The hydrophobic properties of Ag-RCM were tested by a contact angle analyzer. The contact safety of the Ag/AgCl electrode and Ag-RCM electrode was tested by wearing them on the arm for 5 hours. The Ag-RCM electrode was washed three times in water for two minutes each time and repeated five times to measure its electrochemical stability.

ECG tests

The Ag-RCM electrodes are used as electrodes for the commercial ECG device (BDM101) to test the ECG signals of the volunteers. The digital signal is transmitted to the PC via Bluetooth and then the signal is

Results And Discussion

3.1 Design and synthesis process of Ag-RCM

Figure 1a shows the design and preparation process of the Ag-RCM. Cellulose was dissolved with [Bmim]Cl to prepare RCM, and then the dried ones were prepared into Ag-RCM composite conductive films by electroless plating. First, treated cotton fibers were added to the liquid system of melted [Bmim]Cl. Cl^- and hydrogen on the hydroxyl group in the cellulose macromolecular chain form hydrogen bonds, thus breaking a large number of hydrogen bonds existing between the macromolecular chains in cellulose, and imidazole cations form hydrogen bonds with the smaller spatially-restricted cellulose-based oxygen atoms via aromatic hydrogen, eventually leading to cellulose dissolution (Ding et al. 2012; Pinkert et al. 2010). Therefore, at the beginning of dissolution, a large number of fibers could be seen with the optical microscope, and over time, when the cotton fibers were completely dissolved, no fibers could be observed under the optical microscope (Figure 1b). When the cellulose was completely dissolved by [Bmim]Cl, the preparation of regenerated cellulose hydrogels was obtained by the immersion gelation method using deionized water as a coagulation bath.(Ma et al. 2017) (Figure 1c). The reason for precipitation is the competitive hydrogen bonding between water and cellulose hydroxyl groups(Sun et al. 2009). In this way, the ionic liquid was replaced and the regenerated cellulose hydrogel was formed. Next, the regenerated cellulose hydrogel was wrapped with absorbent paper and pressed with a heavyweight for 24 hours to obtain a flat and transparent RCM (Figure 1d). When RCM is added to the PdCl_2 solution, the cellulose membrane with high specific surface area will adsorb palladium chloride ions and form activation centers. After putting the activated RCM into the silver ammonia solution with sufficient stirring, a very small amount of Ag^+ in the solution can form coordination bonds between the polar hydroxyl groups of cellulose and the electron-rich oxygen atoms on the ether group. Then glucose solution was added as a reducing agent. According to the reduction potential of palladium ion is lower than that of silver ion, palladium ion is firstly reduced to palladium particles, which catalyze the reduction of Ag^+ (Ye et al. 2007). Finally, after electroless plating, the flexible Ag-RCM is obtained as shown in Figure 1e.

3.2Chemical structure and morphology of the composite films

Electrode sheets collect ECG signals by converting ionic currents in living organisms into electronic currents, which in turn are useful for analyzing human health conditions. The resistance and conductivity of the electrode affects the electrode to monitor the ECG signal. Therefore, the resistance and conductivity of the electrodes must be tested and the results are shown in Figure 2. The resistance of Ag-RCM gradually decreased from 21.6 Ω to 0.44 Ω as the concentration of AgNO_3 increased (Fig. 2a). The conductivity of the Ag-RCM electrode also gradually increased from 11.57 s/cm to 252.53 s/cm (Fig.2b). The resistance of the Ag-RCM electrode had a much lower resistance and a much higher conductivity than the other electrodes, which helped to ensure that the electrodes monitored a high-quality ECG signal.

FTIR spectra of cellulose (CEL), RCM, and Ag-RCM samples were obtained by using FTIR system (FTIR, Nicolet 6700, USA) in the frequency range of $500\text{--}4000\text{ cm}^{-1}$, and the results are shown in Figure 2c. The comparison shows that the spectra of RCM and CEL are almost identical, no new functional groups are produced, and there is no disappearance of functional groups, only the intensity and wavenumber of the peaks are different, which indicates that there is no chemical reaction occurring during the dissolution and solidification bath of cellulose, and there are only physical changes during the whole process (Yu et al. 2018). This further proves that [Bmim]Cl can dissolve cellulose directly. The absorption peaks at 3354 cm^{-1} , 2900 cm^{-1} and 1060 cm^{-1} correspond to the -OH, -CH₂ and C-O-C stretching vibration peaks in the cellulose molecule (Johar et al. 2012; Kuo and Lee 2009; Oh et al. 2005), respectively, as can be seen from the figure 2c. The peak near 3354 cm^{-1} is the -OH vibrational peak, there is a large amount of -OH in cellulose, so the peak at 3354 cm^{-1} is high and strong, after dissolution by [Bmim]Cl, the peak is weak and moves to a lower wavenumber, indicating that the hydrogen bond is weakened to some extent (Yu et al. 2018). This is due to the fact that during the dissolution of cellulose, the anions and cations of [Bmim]Cl interact with cellulose separately, resulting in a weakening of the -OH interaction between the cellulose macromolecular chains. Cellulose is reconnected by hydrogen bonding during regeneration, a recrystallization process in which molecules are rearranged, hydrogen bonds are reorganized, parts are rearranged and stacked, and the crystallinity of cellulose is slightly reduced.

The thermogravimetric analysis of CEL and RCM was carried out by a thermogravimetric analyzer, and the results are shown in Figure 2d. Comparing the thermal decomposition curves of CEL and RCM, it can be seen that both of them have only three stages of the thermal decomposition process, but the thermal stability of CEL is better, when the temperature reaches about $310\text{ }^{\circ}\text{C}$, it starts to decompose gradually, and the weight loss rate reaches the maximum at $390\text{ }^{\circ}\text{C}$; while RCM starts to decompose at about $290\text{ }^{\circ}\text{C}$, the weight loss rate reaches the maximum at $350\text{ }^{\circ}\text{C}$, and the decomposition ends at $610\text{ }^{\circ}\text{C}$. From the above data, it can be seen that the thermal stability of cellulose decreases after regenerating with [Bmim]Cl. The reason for the decrease in the thermal stability of cellulose may be related to the breakage of some hydrogen bonds and cellulose macromolecule chains during the dissolution process. Ag-RCM started to decompose at about 210°C , reached the maximum weight loss at 310°C and ended the decomposition at 510°C , which may be due to the good thermal conductivity of silver played a catalytic role in the decomposition of RCM.

Figure 2e shows the XRD spectra of the thin silver layer on the RCM. It can be seen that the positions of the diffraction emission peaks at $2\theta = 38.16^{\circ}$, 44.28° , 64.42° , 77.47° , and 81.53° with JCPDS card 04-04-0783 are in general agreement, corresponding to the (111), (200), (221), (311), and (222) planes, respectively. These peaks correspond to the face-centered cubic structure of Ag. The peaks are sharp and the particles are pure and free of impurity ions.

The morphologies of RCM and Ag-RCM composite films were observed by field emission scanning electron microscopy as shown in Fig 3. The surface of RCM was very flat at low resolution (Fig. 3a), while there was still a rough structure at high resolution (Fig. 3b). This may be due to the loss of moisture

during the press-drying process (Kato et al. 2019), which causes crumpling of the RCM. Or it could be the effect of surface tension (Alawiye et al. 2019), which causes the wrinkling of RCM. It could also be the faster exchange rate of deionized water and [Bmim]Cl, which causes wrinkles on the surface of the RCM membrane. After electroless plating, a large number of silver particles were deposited on the surface of RCM, and the surface of Ag-RCM was rough and dense in structure (Fig.3c~d). This is because the deposition of silver particles makes the original rough structure more obvious, but a large number of pore structures can be observed at high resolution (Fig.3e~h), which is due to the agglomeration of silver particles (Mackus et al. 2016), resulting in the interconnection of silver clusters to form pore structures. The porosity of the Ag-RCM surface gradually decreased with the increase of AgNO₃ use concentration, which is because the silver particles on the RCM surface gradually increased with the increase of silver nitrate concentration. The pores on the surface of 0.05 mol/L Ag-RCM are smaller and more numerous than those on the surface of 0.2 mol/L Ag-RCM.

3.3Ag-RCM electrodes electrical performance tests

The bioelectric signal is derived from the difference in ion concentration inside and outside the cell membrane. When the cardiomyocyte receives stimulation, the ion channels on the cell membrane open, resulting in differences in ion concentrations inside and outside the cell membrane, and the ECG signal is transmitted to the body surface through human tissues, sensed by electrodes, amplified at the back end, and processed by signal acquisition circuits. The electrode plays a key role as a sensor during the electrode acquisition of ECG signal, and the basic principle of sensing is the electrochemical reaction at the electrode skin interface, which makes the exchange of ions and electrons occur. As shown in Figure 4a, to the metal electrode and electrolyte contact will occur electrochemical decay candle, electrode material in the form of ions into the electrolyte, electrons remain in the metal body, this process is reversible, the electrochemical reaction equation as shown in equation (1) and equation (2). The electrical properties of this electrochemical interface can be represented by a classical electrochemical equivalent circuit, as shown in Figure 4b. The AC impedance of the electrode electrolyte interface can be expressed as equation (3).

$$|z| = R_s + \frac{R_d}{1+j\omega C_d} \quad \omega = 2\pi f \quad (3)$$

Where ω is the angular frequency and f is the frequency. From Figure 4b and equation (4), it can be seen that at high frequencies, C_d is the path, R_d is the short circuit, and the impedance of the equivalent circuit is $|z|=R_s$; at low frequencies, C_d is the break, and the impedance of the equivalent circuit $|z|=R_s+R_d$; throughout the frequency range, the higher the frequency, the lower the impedance.

Figure 5 shows the impedance spectra, EIS and open-circuit voltages of Ag-RCM electrodes prepared with different concentrations of AgNO_3 and commercial Ag/AgCl electrodes, which monitored by using an electrochemical workstation. During prolonged wear of the electrode, sweat secreted by sweat glands accumulates between the electrode and the skin, which acts as an electrolyte, so a 20 g/L NaCl and 1 g/L urea solution was used as a simulated sweat solution for skin-electrode impedance testing (Wang et al. 2021b). The working electrode is a prepared Ag-RCM electrode specimen of size $1.2 \times 1.0 \text{ cm}^2$, the counter electrode is a large area platinum screen, and the reference electrode is a glymeric acid electrode reference electrode. The electrochemical impedance spectrum was scanned at 10 mV and the scanning frequency range was from 0.01 Hz to 1000 Hz. As can be seen in Figure 5a, the skin-electrode contact impedance curves of the Ag-RCM electrode and the Ag/AgCl electrode were similar. This is because when the skin forms a conformal contact with the electrode, the skin-electrode contact impedance is mainly determined by the skin rather than the electrode (Zhang et al. 2020). The skin-electrode contact impedance curves for 0.15 mol/L Ag-RCM and 0.2 mol/L Ag-RCM largely overlapped with those for Ag/AgCl electrodes. It was only about $8 \text{ k}\Omega / \text{cm}^2$ at 700 Hz. The skin-electrode contact impedance of 0.05 mol/L Ag-RCM and 0.1 mol/L Ag-RCM was slightly higher, but only $18 \text{ k}\Omega / \text{cm}^2$ at 700 Hz. Therefore, Ag-RCM can be a good substitute for Ag/AgCl electrodes for monitoring ECG signals. The open-circuit voltage affects the potential of the ECG test and can have an impact on the accuracy of the results, so the open-circuit voltage of the Ag-RCM electrode needs to be tested. The open-circuit voltage has a scan time of 30 seconds, a sampling interval of 0.1 seconds, and a high potential of 1 V and a low potential of -1 V. The open-circuit voltages of Ag-RCM electrodes prepared with different AgNO_3 concentration are shown in Figure 5b. It can be seen that the open-circuit voltages of all electrodes were relatively stable with time and fluctuated only within a small range. The open-circuit voltages of the 0.05 mol/L Ag-RCM and 0.10 mol/L Ag-RCM electrodes showed almost no fluctuation, the open-circuit voltages of the 0.15 mol/L Ag-RCM electrode fluctuated between 0.07 mV and 0.081 mV, and the 0.2 mol/L Ag-RCM electrode fluctuates between 0.06 mV~0.08 mV. Therefore, there is little effect on the detection of ECG signals.

EIS is used to analyze the electron transport and diffusion of the electrodes. The open-circuit voltage of each electrode was first measured, and then the test was performed by setting the scanning frequency from 0.01 Hz to 1000 Hz. The results of the EIS measurements were presented as Nyquist plots. The Nyquist curves of all Ag-RCMs were approximately straight lines (Fig. 5c~f), even in the high-frequency region, and the slope of the Nyquist curves gradually increased with increasing concentration of AgNO_3 used. This indicates that the faster the ion diffusion rate at the interface between electrode and electrolyte (Zhang et al. 2018).

3.4 Ag-RCM electrode stability tests

The stability of the electrodes is also important for the long-term monitoring of ECG signals. Ag-RCM electrodes are not only hydrophobic (Fig. 6d), but the silver is chemically stable and does not react with oxygen, water, etc. in the air. This facilitates the preservation of the electrode for a long time.

For longer ECG monitoring, the comfort and safety of the contact between skin and electrode are also very important. Compared with gel electrodes, Ag-RCM electrodes are softer and biocompatible for long-term ECG monitoring. The Ag-RCM electrodes, gel electrodes were fixed on the arm for 5 hours and then removed. It is obvious that there is a clear indentation in the skin under the gel-assisted electrode (Fig. 6a). However, the skin under the Ag-RCM electrode was almost unchanged (Fig. 6b). Examination of the impedance showed that the impedance of the Ag-RCM electrodes after 5 h of wear was almost no different from that of the unused Ag-RCM electrodes (Fig. 6e). Unlike wet electrodes, which become dehydrated and dry over time, Ag-RCM electrodes do not. Therefore, Ag-RCM electrodes can be used for prolonged ECG monitoring. The Ag-RCM electrode was washed underwater for 30 seconds, then dried naturally and repeated five times. As shown in Figure 6f, the impedance of the electrodes changed very little. Therefore, the Ag-RCM film has good stability to environmental changes as a good ECG electrode.

3.5 Performance of Ag-RCM electrodes in ECG monitoring

The electrodes are designed in the form of a wristband for long-term monitoring of ECG signals. The wristband is a small piece of fabric consisting of Velcro straps, Velcro straps and an electrocardiograph. As shown in Figure 7b, the wristband is made of two long pieces of cotton fabric, a set of metal concealed buckles and a metal buckle sewn together. The ECG signal was monitored by using a commercially available BMD101 device (Fig. 7a). Before monitoring the ECG signal with Ag/AgCl, the skin needs to be treated to reduce the resistance caused by the stratum corneum, whereas with dry electrodes no skin treatment is required and monitoring is performed directly. A volunteer with no history of heart disease was monitored for ECG signals. Prior to monitoring, the volunteer was told to avoid unnecessary exercise and to sit still for 10 minutes prior to the measurement to reduce the effect on the quality of the ECG signal. Electrodes were located on the wrists of the sedentary subjects and were used to monitor the ECG signal. The obtained ECG signals were transmitted via Bluetooth (Fig. 7b) to the computer side of the BMD101 ECG monitoring device and filtered using MATLAB2018. The Ag-RCM electrodes prepared with different concentrations of AgNO_3 all obtained clear and stable ECG signals (Fig. 7c~f), all P, Q, R, S and T waves were clearly visible, and the monitored ECG signals contained much less noise than those of the commercial electrodes (Fig. 7g). However, as the concentration of AgNO_3 used increased, the noise waves increased significantly, indicating that the more silver particles deposited is not the better. This is because as the number of deposited silver particles increases, the network structure of the silver layer gradually decreases, reducing the electron mobility performance. This indicates that the Ag-RCM electrode can replace the conventional Ag/AgCl electrode.

Conclusions

In this work, we prepared a regenerated cellulose composite film and electroless plated with silver layer on the surface. By controlling the amount of AgNO_3 , the skin-electrode contact impedance of the Ag-RCM can be controlled. The ECG signals monitored by all Ag-RCM were clearer and more stable than those of commercial Ag/AgCl electrodes. The skin-electrode contact impedance was similar to that of commercial Ag/AgCl. The impedance at 700 Hz is only $8 \text{ k}\Omega/\text{cm}^2$, and the conductivity can reach 252 S/cm (when

AgNO₃ was used at a concentration of 0.2 mol/L). After 5 hours of wear, the skin contact impedance of the electrode was only 10 kΩ/cm² (when AgNO₃ was used at a concentration of 0.20 mol/L). The maximum fluctuation range of the open circuit voltage of the electrode is only 0.02 mv. In addition, the Ag-RCM electrode is comfortable to wear and will not incur skin allergy problems as conventional wet electrodes do. We believe that the method of this Ag-RCM films electrode can provide some new insights to the exploration of low-cost dry electrodes and monitoring devices.

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Figures

Figure 1

a Schematic diagram of the preparation process of RCM. b Cellulose dissolution before and after magnification 100 times under an optical microscope. c Cellulose hydrogel. d RCM. e Ag-RCM

Figure 2

a Resistance of Ag-RCM electrodes. b Conductivity of Ag-RCM electrodes. c FTIR spectra of CEL, RCM. d Thermogravimetric curves of CEL, RCM, Ag-RCM. e XRD pattern of thin silver layers

Figure 3

a-h SEM images of the films. a RCM at low resolution. b RCM at high resolution. c Ag-RCM at low resolution. d Ag-RCM at high resolution. e~h Particle size of Ag-RCM at the same resolution

Figure 4

a Ion exchange at the electrode and skin (electrolyte) interface. b Electrical equivalent circuit model of the electrode and electrolyte interface.

Figure 5

a The skin-electrode contact impedance of the Ag-RCM electrodes and Ag/AgCl electrode. b Open circuit voltage of Ag-RCM electrodes. c-f Nyquist plot of 0.05mol/L, 0.10mol/L, 0.15 mol/L, 0.20 mol/L Ag-RCM electrodes. Inset a magnified of the high-frequency region

Figure 6

a Ag/AgCl electrode after 5 h of wear. b Ag-RCM electrode after 5 h of wear. c Contact angle of RCM. d Contact angle of Ag-RCM. e Impedance of Ag-RCM electrode after 5 h of wear. f Impedance of Ag-RCM electrode after washing.

Figure 7

a Photograph of the PC software used for real-time monitoring of ECG curves. b Photographs of the 0.05 mol/L Ag-RCM electrode and the analog front-end circuit. c-g ECG profiles obtained from 0.05 mol/L to 0.20 mol/L Ag-RCM electrode.