JOM, Vol. 68, No. 4, 2016
DOI: 10.1007/s11837-016-1818-0

Nanomaterial-Enabled Dry Electrodes for Electrophysiological Sensing: A Review

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Long-term, continuous, and unsupervised tracking of physiological data is becoming increasingly attractive for health/wellness monitoring and ailment treatment. Nanomaterials have recently attracted extensive attention as building blocks for flexible/stretchable conductors and are thus promising candidates for electrophysiological electrodes. Here we provide a review on nanomaterial-enabled dry electrodes for electrophysiological sensing, focusing on electrocardiography (ECG). The dry electrodes can be classified into contact surface electrodes, contact-penetrating electrodes, and noncontact capacitive electrodes. Different types of electrodes including their corresponding equivalent electrode–skin interface models and the sources of the noise are first introduced, followed by a review on recent developments of dry ECG electrodes based on various nanomaterials, including metallic nanowires, metallic nanoparticles, carbon nanotubes, and graphene. Their fabrication processes and performances in terms of electrode–skin impedance, signal-to-noise ratio, resistance to motion artifacts, skin compatibility, and long-term stability are discussed.

Key words: Nanomaterials, Dry electrodes, Electrocardiogram (ECG), Electrophysiological sensing

INTRODUCTION

Cardiovascular diseases are among the leading causes of death.[1,2] Continuous monitoring of the heart activities through electrocardiogram (ECG) plays an indispensable role in the prevention, early detection/diagnosis, management, and postoperative treatment of cardiovascular diseases. The recording of ECG and other key vital signs (e.g., blood pressure and blood glucose) are usually performed in a hospital for a short period of time. However, the high cost of hospital-centered care and the benefits of long-period recording have driven significant interest toward homecare,[3,4] which could be realized with the development of wearable devices and wireless communications. To satisfy the requirements for wearable long-term monitoring, the ECG electrodes and acquisition systems should be lightweight, biocompatible, easy to use, comfortable to wear, and capable of maintaining good signal quality during daily activity and over a long period of time.

Disposable pregelled Ag/AgCl electrodes are widely used so-called "wet electrodes," which rely on the conductive gel to maintain good electrical contact with skin but suffer from signal degradation as the gel dehydrates with time. New gel has to be applied, which is inconvenient and sometimes infeasible. In addition, studies have showed that long-term use of gel on the skin can potentially provoke dermal irritation and allergic reactions.[5–7] The adhesive used in Ag/AgCl wet electrodes can trigger chemical irritation and cause pain due to skin fragments during the mechanical peeling process.[8,9] Moreover, due to the high impedance to the electrode, stratum corneum is often abraded to reduce its thickness. Owing to these concerns, researchers are seeking alternative electrodes that can eliminate the gel and even skin preparation but achieve high signal quality over a long time.

Relative movement of the electrode to skin represents the main source of the motion artifacts. Flexible/stretchable dry electrodes that can form intimate contact with the curvilinear surface of skin could greatly suppress the movement of the electrodes and reduce the motion artifacts as a result. Nanomaterials possess unique properties such as high surface area, excellent electrical conductivity, and superior flexibility, and they have been extensively explored as the flexible/stretchable devices for wearable applications, such as display, transistors, sensors, actuators, and energy storage devices.[10] The application of nanomaterial-based dry electrodes for long-term ECG monitoring has received much interest recently as substitutes for traditional pregelled Ag/AgCl ones. This article provides a review of the recent advances of nanomaterial-enabled dry ECG electrodes, including contact surface electrodes, contact-penetrating electrodes, and noncontact capacitive electrodes. Before discussing nanomaterial-based dry electrodes, an overview of different types of electrodes, their electrode–skin interface modals, and the sources of noise is first provided. Subsequently, the recent progress on nanomaterial-enabled dry ECG electrodes is summarized. Although this article is focused on ECG sensing, these dry electrodes can also be applied for other electrophysiological sensing, such as electromyography (EMG) and electroencephalography (EEG).

ECG ELECTRODE AND ELECTRODE–SKIN MODEL

Sequential depolarization and repolarization of the heart generates tiny electrical fluctuations in the human body that arise from the movement of ions. A typical ECG tracing for one cardiac cycle consists of three major electrical entities, where the P wave is generated by the depolarization and contraction of the atria, the QRS complex represents the depolarization of the ventricles, and the T wave is created by the repolarization of the ventricles.[11,12] An ECG records such repeating potential variations over a period of time, which is achieved by placing two or more ECG electrodes on the body in an appropriate position and recording the differential voltage between them using an acquisition device. There are a total of 12 leads (6 limb leads and 6 augmented limb leads) that indicate 12 different vectors onto which the electrical activity of the heart is projected. An ECG electrode, either a pregelled wet electrode or a dry electrode, serves as a transducer to convert the ionic current in the human body to electrical current in the electrode. In theory, the transduction can be either polarizable or nonpolarizable.[13] For a polarizable electrode, no actual current flows but only displacement current is involved and the electrode behaves like a capacitor. For a nonpolarizable electrode, direct current flow is allowed and the electrode behaves like a resistor. In practice, the behavior of an actual electrode lies between these two extremes. The capacitive electrode is more polarizable, and the pregelled Ag/AgCl electrode is more like a nonpolarizable electrode. The electrode–skin contact impedance is commonly used to evaluate how effective the charges are transferred from the body to the electrode.[14]

Pregelled Wet Electrode

Disposable pregelled Ag/AgCl wet electrodes are widely used to capture the ECG signals due to their low cost and good performance. The equivalent electrode–skin interface model[13] is presented in Fig. 1a. A half-cell potential is formed at the electrochemical electrode–electrolyte interface, and the potential is denoted by E_{hc}. The double-layer structure of the interface is modeled by a capacitor C_{d} and a resistor R_{d} placed in parallel, where the resistor describes the leakage resistance across the two layers. Since the gel contains a high concentration of ions, a resistor R_{g} is included to denote its resistance. Skin is a layered structure consisting of primary layers of epidermis, dermis, and subcutaneous tissues. The dermis and subcutaneous tissues, mainly composed of blood vessels, nerves, preparatory glands, and hair follicles, can be treated as a pure resistor R_{u}, whereas the epidermis exhibits capacitive and resistive behavior and can be modeled by a parallel circuit consisting of C_{e} and R_{e}.[15] The outermost layer of epidermis is stratum corneum, which is composed of dead cells and is therefore electrically insulating. The behavior of the stratum corneum is dynamic since it can regenerate itself in a short time. In addition, the stratum corneum serves as a barrier to protect the underlying layers and is semipermeable to ions. A difference in ionic concentration across the stratum corneum results in a potential E_{se}.[13]

Dry Electrode

Without the electrolytic layer, the dry electrode eliminates the signal degradation due to dehydration of the gel and the concerns regarding dermatological responses. The dry electrodes can be divided into contact and noncontact electrodes and further classified into three categories depending on the coupling between the electrode and skin: surface electrodes that are in direct contact with only the skin surface, penetrating electrodes that punch into the skin, and capacitive electrodes that indirectly contact the skin through an insulating layer.

Dry Surface Electrode

For nonobtrusive surface electrodes, due to the absence of the conductive gel, the coupling between the electrode and the skin is capacitive. The electrodes, especially rigid electrodes, cannot totally adapt to the rough skin surface, leading to inevitable air bubbles/gaps in between, which functions like a dielectric layer.[16] The skin humidity and sweat accumulated under the electrode cause resistance between the electrode and the skin. As a result, the electrode–skin interface is modeled by a

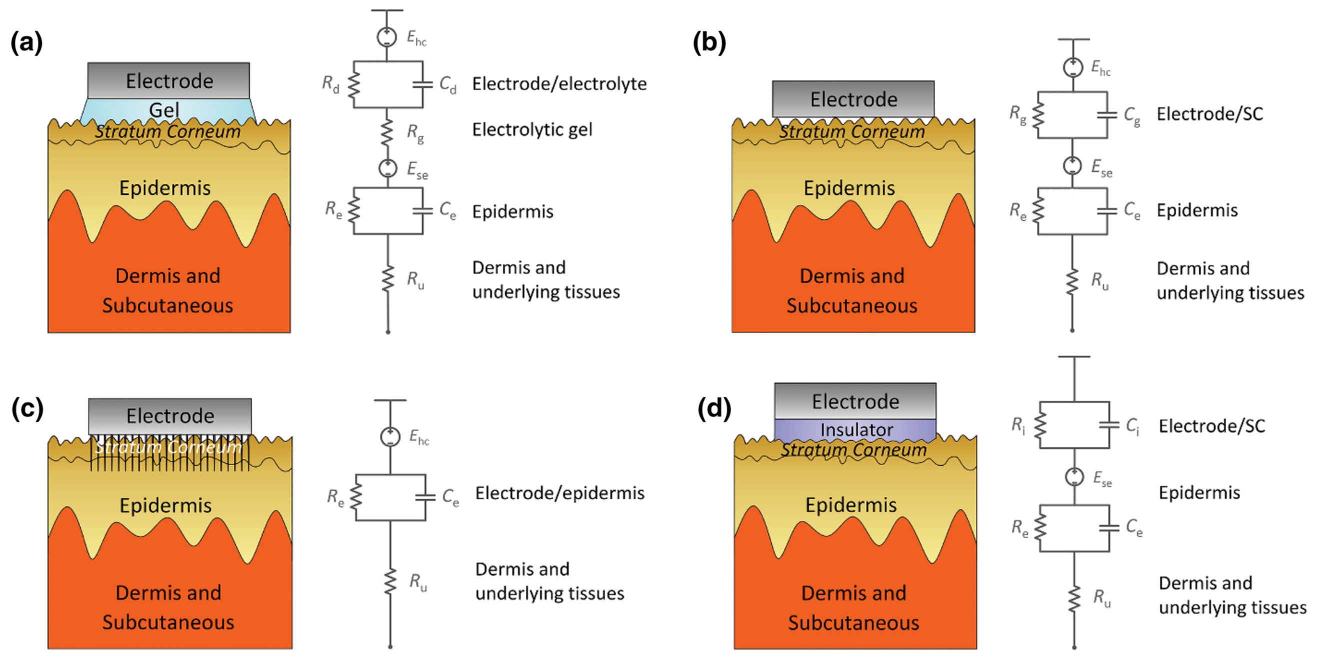

Fig. 1. Schematics and corresponding electrode–skin interface models for (a) pregelled wet electrode, (b) dry surface electrode, (c) dry penetrating electrode, and (d) dry capacitive electrode.

parallel connected capacitor C_g and resistor R_g, as shown in Fig. 1b.[8,16] Since skin humidity and sweat have a similar, although less effective function to the electrolyte, a half-cell potential E_{hc} is included to describe their interface with the electrode. The electrode–skin impedance for the dry surface electrode is larger than that for the wet electrode due to the relatively poor contact with skin. The electrode–skin interface impedance is highly dependent on applied pressure, the humidity of the skin, and the presence of other fluids that can moisturize or improve the conductivity of skin. Applying pressure improves the contact, and therefore, it decreases the contact impedance.[16–18] A high skin humidity/hydration level reduces the overall skin impedance by increasing both the conductivity and the dielectric constant of skin.[19,20] Typically, after applying the dry electrode for a few minutes, the electrode–skin impedance tends to decrease due to the perspiration built up under the skin. Even simply applying a few drops of water can effectively reduce the interface impedance.[21] It is thus expected that the motion artifacts of dry electrodes is initially high upon applying the electrodes on skin, but it decreases and reaches a level even lower than that of pregelled electrodes after a certain settling time.[22]

Dry surface electrodes made of stiff materials[8,23] are difficult to conform to the skin, leading to variation of the contact area under motion and as a result high interface impedance and high motion artifacts. Several ways were developed to fabricate flexible surface electrodes: depositing metal thin film on flexible substrate,[24–27] mixing conductive fillers into a polymer matrix as polymer composites,[28,29] patterning serpentine metal mesh on thin silicone to form tattoo-like electrodes,[30] and fabricating textile-integrated electrodes[31,32] by metal electroplating,[33] screen printing,[1,18,34,35] and knitting/weaving conductive yarns into fabrics.[36–38] Flexible surface electrodes, compared to rigid ones, can better adapt to the skin topology, the curvature, and the hairs, and thus, they can achieve a more comfortable, stable interface with lower impedance.[25,27]

Dry Penetrating Electrode

Penetrating electrodes that pierce into the surface of the skin represent another kind of dry contact electrode. The influence of the unstable and insulating stratum corneum can be effectively minimized.[15] Since typically only stratum corneum is penetrated, which is formed by dead cells, this method is considered to be painless and minimally invasive. The electrical model is given in Fig. 1-c.[39,40] The spikes/needles are in direct contact with the conductive layers in epidermis below the stratum corneum such as stratum germinativum, which has a similar function to the gel. Besides the resistance of the conductive dermis and underlying tissues, only the coupling of the electrode and the conductive layers in epidermis is present, which is described by a half-cell potential and a resistor R_e and a capacitor C_e connected in parallel. Micromachined sharp spikes,[14,40,41] barbed microtip arrays,[39] and hollow microneedle arrays[42] have been designed to penetrate the skin surface for electrophysiological (or biopotential) measurements. Although claimed to be minimally invasive, the skin biocompatibility and the mechanical and electrical stability of the electrodes for long-term applications need to be further investigated.

Dry Capacitive Electrode

A capacitive electrode does not have direct electrical contact with skin. It is either isolated with an insulating layer and having a physical contact with skin or coupled with the skin in a noncontact manner with air, clothing, or other materials between the electrode and the skin. The contribution of the air/clothing or other dielectrics is described by a capacitor C_i and a resistor R_i in parallel (Fig. 1d).[4] Such capacitive electrodes eliminate the risk of skin irritation and are electrically safe, easy to be cleaned and reused, and ready to be integrated with textiles.[43] For example, with the capacitive electrodes, an ECG has been recorded in a bathtub,[44] in bed during sleeping,[45] through a car seat to evaluate a driver's stress,[46] through a wheelchair,[47] or from clothing.[48,49] The capacitive electrodes are generally prone to the motion artifacts and moving charges presented near the electrodes. But if properly shielded and buffered, the capacitive electrodes can perform in a manner as well as pregelled electrodes in terms of contact impedance and resistance to interference and motion artifacts.[22]

SOURCES OF NOISES

Due to the low amplitude of electrophysiological signals, the measurements could suffer significantly from noises. For both pregelled wet electrodes and dry electrodes including nanomaterial-based dry electrodes, the noises can be classified into two categories: contact noise and environment noise.[50,51] The environment noises associated with biopotential measurements include amplifier noise and interference noise, the latter of which is more prominent. The 50/60-Hz powerline interference originated from ac power line potential is capacitively coupled to the bioelectric signals through the electrode leads, or through the human body, converting the common mode signals to differential signals.[22,52] The charge sensitivity due to moving electric charges poses another problem. Techniques such as shielding, active electrodes using buffer at the electrode site, contact impedance match, and driven-right-leg (DRL) circuits are developed to reduce the interference.[8]

Contact noises, arising from the disturbance in interfaces (such as the gel–skin and the gel–electrode interface)[53], contribute to a significant part of the signal noises. Relative motion of electrodes to the body, including vertical separation and transversal slipping and friction, disturbs the charge distribution at the interfaces and thus introduces motion artifacts.[3,4] Mechanical stretching of the skin that changes the skin potential[13,54] represents another source of motion artifacts. Thermal noise and the presence of other biopotentials such as the electromyogram (EMG) signals can introduce additional noises.

Flexible/stretchable electrodes that can maintain good contact with skin even under motion are promising to greatly reduce motion artifacts. The interference can be effectively reduced if the electrodes are shielded and buffered, and they are placed away from muscles to mitigate the influence of EMG.[8] Moreover, attaching the electrode with an appropriate pressure to stabilize the contact[3] on a relatively moisturized skin (e.g., by sweat accumulating or applying water or moisturizer)[22] can further alleviate the motion artifacts.

NANOMATERIAL-ENABLED DRY ECG ELECTRODE

The excellent compliance of the nanomaterial-based electrodes allows for good wearability, better contact with the curvilinear surface of the skin, and reduced motion artifacts. As a result, nanomaterial-enabled dry ECG electrodes are attractive candidates for long-term ECG sensing. This section reviews the recent progress of the nanomaterial-enabled dry ECG electrodes, including contact surface electrodes, contact-penetrating electrodes, and noncontact capacitive electrodes. Their performances are benchmarked against the commercial pregelled ones.

Contact Surface Electrode

Metallic Nanomaterials

Metallic nanomaterials, such as nanoparticles and nanowires (NWs), are attractive materials for dry biopotential electrodes due to their high electrical conductivity. Hoffmann and Ruff reported flexible dry electrodes for ECG and surface EMG recordings using dispersed nanoparticles in polysiloxane (Fig. 2a).[55] Two approaches of textile integrations, functional sport shirt and flexible belt with ECG electrodes and stud connectors, were realized, as illustrated in Fig. 2b and c, respectively. The long-term monitoring feasibility was evaluated in terms of the biocompatibility (according to ISO 10993), skin irritation, and signal quality in comparison to commercial wet electrodes. Comparable electrode-to-skin impedance was achieved after applying the electrode for 10 min owing to the accumulation of sweat. Additionally, the recorded ECG signals showed comparable signal quality and signal-to-noise ratio. The reported dry electrodes were biocompatible and biostable: (1) no irritant effects, no leachable substances released, and no indication of skin sensitization were observed during 30 days of exposure of the material to healthy skin; and (2) no dermal irritation was provoked for wearing the electrode over 8 days. Moreover, the electrodes were machine washable with no sign of performance change, which makes them suitable for long-term applications. As another way to incorporate nanoparticles into textiles, Patel

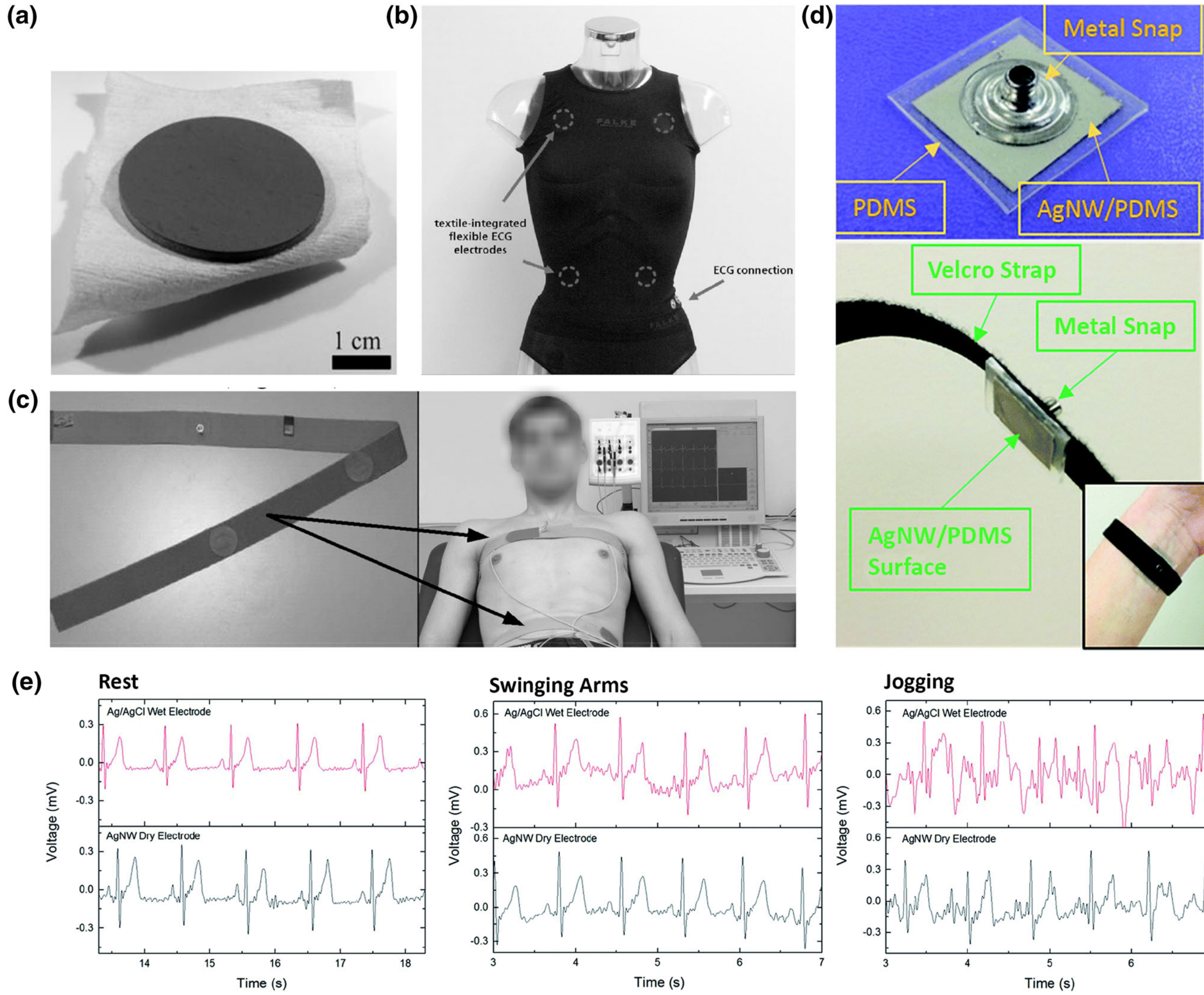

Fig. 2. Dry surface electrodes based on metallic nanoparticle/nanowire composites. (a) Photograph showing a flexible dry electrode made from nanoparticle-loaded polysiloxane. Textile integration of flexible dry electrodes: (b) Functional sport shirt integrated with 4 electrodes and stud connectors. (c) Flexible ECG belt integrated with 3 electrodes. (a–c) Reproduced with permission.[55] Copyright 2007, IEEE. The photo in (c) has been altered at the request of the rightsholder. (d) Top: Photograph of an AgNW/PDMS dry electrode with a metal snap for connection. Bottom: AgNW/PDMS dry electrode integrated with a Velcro strap for attachment to the wrist. The inset shows the strap on the wrist. (e) Comparison of ECG recording of Ag/AgCl wet electrode and AgNW/PDMS dry electrode taken while the subject was seated and resting (left), swinging his or her arms, one degree of movement (middle) and jogging, two degrees of movement (right). (d–e) Reproduced with permission.[17] Copyright 2015, Royal Society of Chemistry.

et al. employed a multi-dip method to load copper nanoparticles inside the polymer matrix of a versatile, low-cost, and stable polypropylene nonwoven fabric.[56] The resulting fabric electrodes were low cost and flexible since only a minimal amount of nanoparticles was introduced.

Our group recently developed a silver NW (AgNW)-based dry electrode[17] for ECG and EMG sensing where the NWs were just embedded below the surface of the polydimethylsiloxane (PDMS) matrix. The electrodes are highly stretchable and conductive with a conductivity of ~5000 S/cm at 50% tensile strain.[57] A Velcro strap was used to attach the electrode to skin as a wristband, as shown in Fig. 2d. The softness and good compliance of the AgNW/PDMS allow the electrodes to maintain a conformal contact with the skin, even under motion. Applying a mild pressure onto the AgNW electrode further improved the contact between the electrode and the skin, leading to a decreased electrode–skin impedance. The AgNW/PDMS dry electrode performed as well as the pregelled Ag/AgCl electrodes when the subject was resting, and it outperformed the pregelled Ag/AgCl electrodes with less motion artifacts when the subject was swinging their arms (one degree of movement) and jogging (two degrees of movement; Fig. 2e). In this work, the AgNWs were solution synthesized.

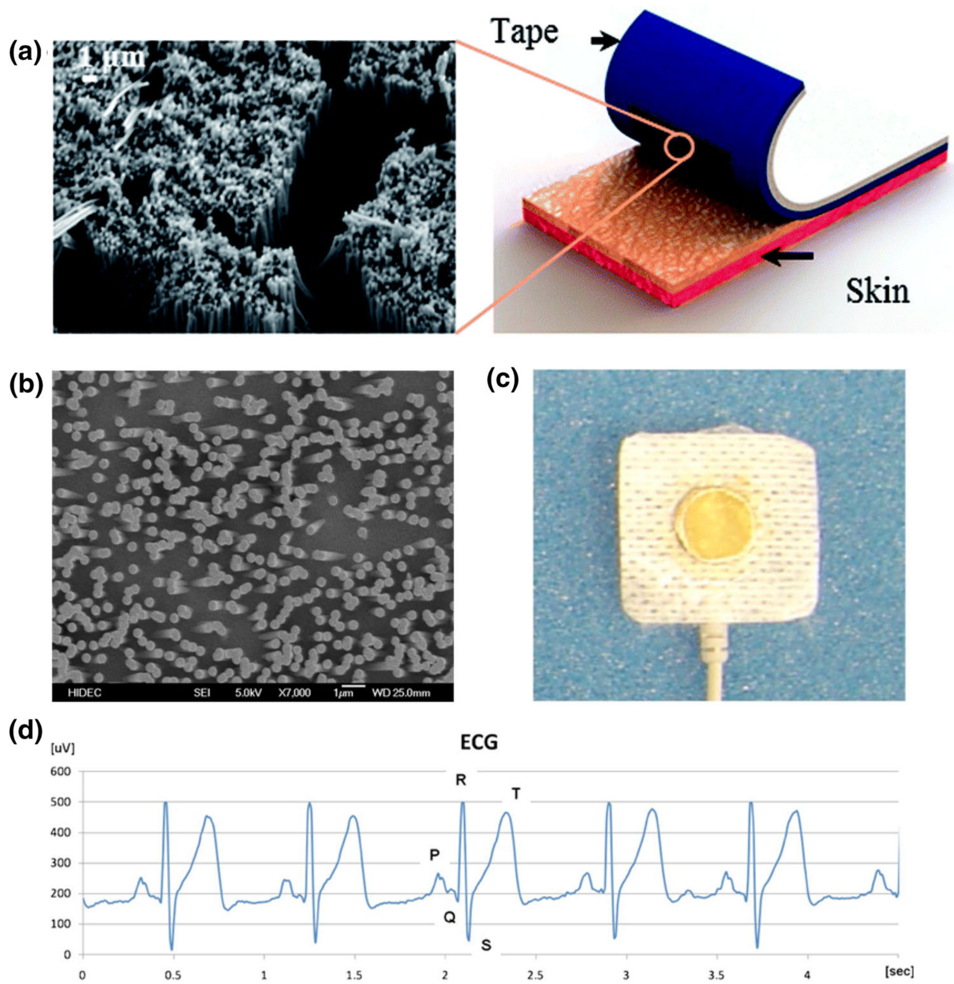

Fig. 3. Dry surface electrodes based on metallic nanowires fabricated by template-assisted electrodepostion. (a) ECG electrode using a high density of platinum nanowires directly grown on a paper substrate. Reproduced with permission.[58] Copyright 2014, Royal Society of Chemistry. (b) SEM image of grown vertical-aligned gold nanowires array. (c) Photograph of the dry electrode based on the vertical-aligned gold nanowires as shown in (b). (d) The recorded ECG signals from gold nanowire-based dry electrode. (b–d) Reproduced with permission.[59] Copyright 2010, ASME.

Besides the solution-synthesized AgNWs, the high density of platinum NWs (PtNWs) and gold NWs (AuNWs) fabricated by applying template-assisted electrodeposition were used to develop dry electrodes. A paper-based dry electrode (Fig. 3a) was prepared using a low-cost and room-temperature process, where a porous anodized aluminum oxide (AAO) membrane was used as the template for electrodeposition of PtNWs and a simple adhesive tape-based method was used to define the electrode pattern without a complex lithography process.[58] Since the high-density NWs were directly fabricated on the paper substrate, the resulting dry electrodes were flexible and foldable. The electrode–skin impedance was measured to be in the range of 100 kΩ to 1 kΩ for frequency from 5 Hz to 1.5 kHz. In another work, a lithography process was used to prepare vertically aligned AuNWs with a polycarbonate nanopore membrane.[59,60] The two-micrometer-long NWs had a dense brush-like shape (Fig. 3b), which can enlarge the effective area in contact with the skin. Both ECG and electroencephalogram (EEG) sensing capabilities were demonstrated along with a low-power and wide data coverage wireless communication system. As shown in Fig. 3d, P wave, QRS complex, and T wave are clearly detectable from the ECG waveforms.

Carbon-Based Nanomaterials

Carbon nanotubes (CNTs) possess high mechanical strength, good electrical conductivity, and can be mass produced at a relatively low cost. To harness their unique properties, CNTs are often dispersed into polymer matrix to make flexible and conductive dry ECG electrodes.[61–63] Due to the large surface area and strong van der Waals interaction between them, CNTs tend to tangle with each other, which makes dispersion of CNT into polymer challenging. Lee and co-workers[62] achieved good dispersion of CNT into PDMS with

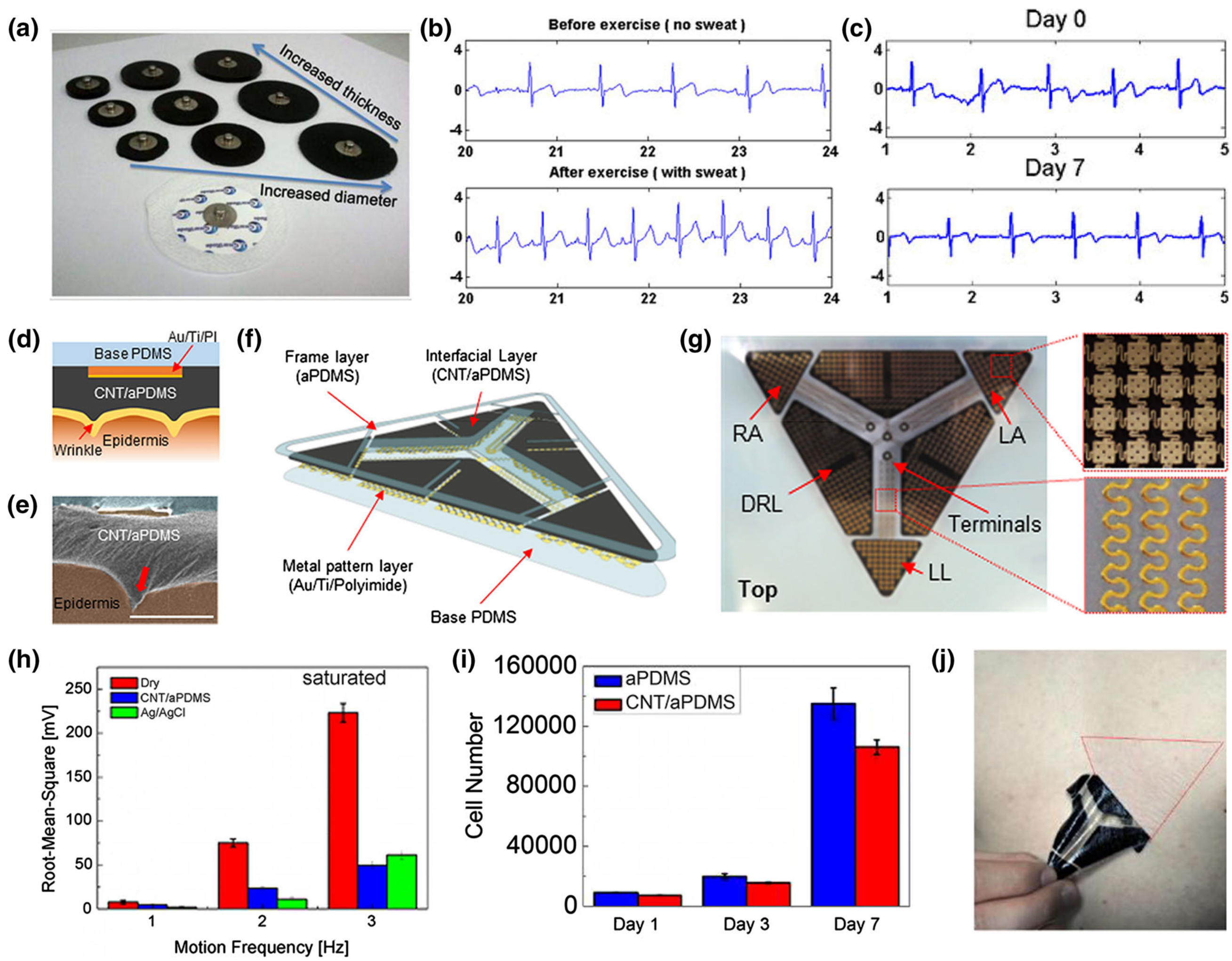

Fig. 4. Dry surface electrodes based on CNT–polymer composites. (a) Photographs of Ag/AgCl pregelled electrode and CNT/PDMS dry electrode with different thickness and diameter. (b) ECG signals measured from CNT/PDMS electrode before (no sweat) and after exercise (with sweat). (c) Comparison of ECG signals measured from CNT/PDMS electrode on day 0 and day 7. (a–c) Reproduced with permission.[62] Copyright 2012, IEEE. (d) Schematic of the self-adhesive electrode in intimate contact with skin. (e) SEM image of a CNT/aPDMS electrode attached to a skin replica, which penetrates the wrinkles of the skin and maintains a conformal contact with wrinkles and rough skin. (f) Schematic showing the structure of a CNT/aPDMS ECG patch. (g) Top view of the self-adhesive ECG patch based on CNT/aPDMS. Cytotoxicity and skin compatibility tests: (h) Results of the live/dead assay for human fibroblast cells cultured on the CNT/aPDMS electrode for a week. (i) The cell number for CNT/aPDMS and aPDMS for days 1, 3, and 7. (j) Photograph of the skin area where the electrode has been attached continuously for 7 days. (d–j) Reproduced with permission.[63] Copyright 2014, Nature Publishing Group.

a wetting and flow stress process. A systematic study of CNT/PDMS composites (Fig. 4a) as dry ECG electrodes was performed to investigate the effects of CNT concentration, effects of the electrode size/thickness, robustness to motion and sweat, and biocompatibility. A higher CNT concentration and larger electrode area gave rise to good signal quality, whereas the thickness of electrodes had minimal effects on the signal quality. The CNT/PDMS electrodes were highly stretchable with good conductivity up to 45% tensile strain. The CNT/PDMS and commercial wet electrodes offered comparable signal quality under various conditions: static, walking (3 km/h), and power walking (5 km/h). No sign of signal degradation was observed after continuously wearing the electrodes after exercise (in the presence of sweat; Fig. 4b) or for 7 days (Fig. 4c). A 7-day in vitro cytotoxicity test showed that the viability of the skin fibroblast cells cultured on CNT/PDMS electrodes exceeded 95%. In addition, no skin irritation was observed after wearing the electrode on the forearms for 7 days.

The same group later hydrodynamically dispersed CNTs into an adhesive polydimethylsiloxane (aPDMS), which enables a thin (120 μm), highly conformal (modulus: 27.5 kPa; skin modulus: 130 kPa), self-adhesive (adhesion force: 1.1 N/cm^2) ECG electrode that can integrate with other electronics through simple soldering (Fig. 4d–g).[63] The self-adhesive ECG patch consists of a PDMS base, an Au/Ti/Polyimide metal layer, an aPDMS frame layer, and a CNT/aPDMS interfacial layer for signal

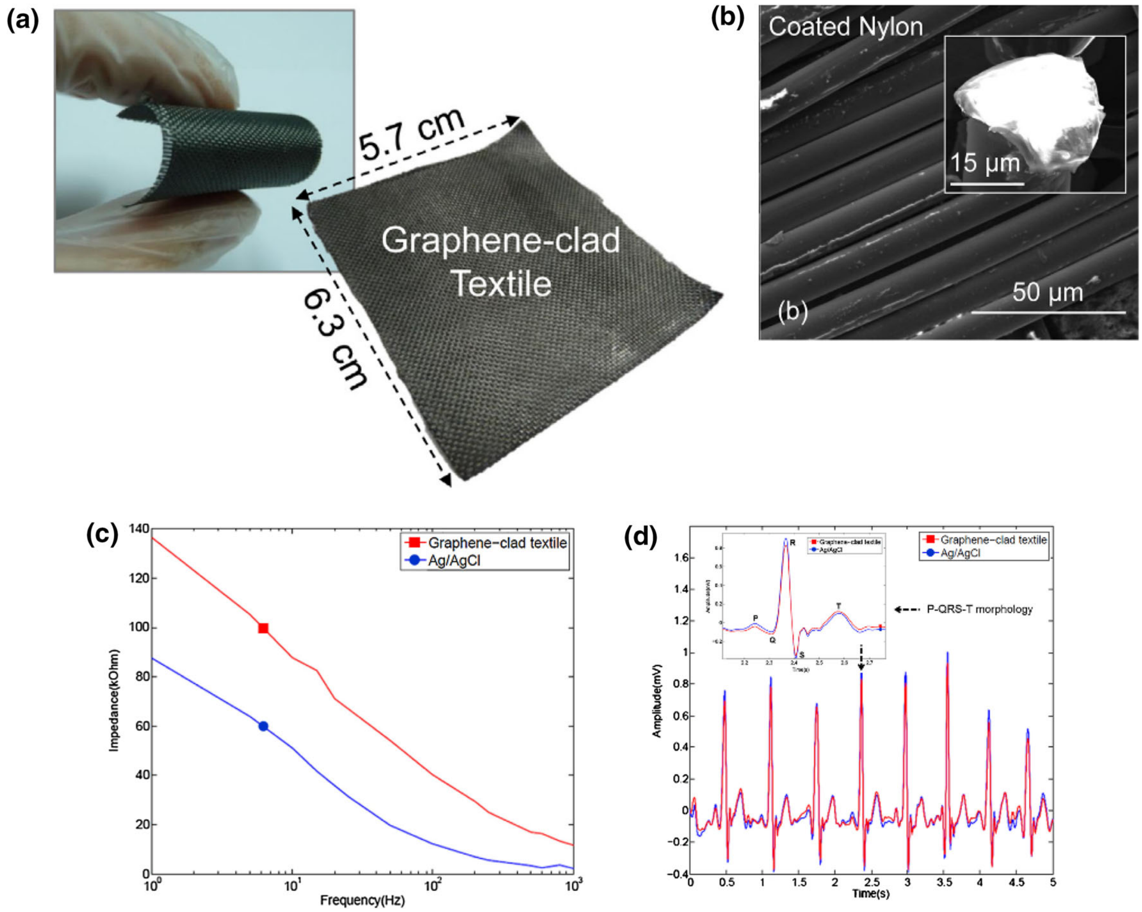

Fig. 5. Dry surface electrodes based on graphene-clad textiles. (a) Photograph of a graphene-coated nylon textile as a dry ECG electrode. (b) SEM image of the graphene-coated nylon fiber. (c) Comparison of the skin–electrode contact impedance as a function of frequency for the graphene-clad textile and pregelled Ag/AgCl electrodes. (d) Comparison of the filtered ECG signals recorded from graphene-clad textile and pregelled Ag/AgCl electrodes. The inset shows the P-QRS-T morphology. Reproduced with permission.[68] Copyright 2015, Elsevier.

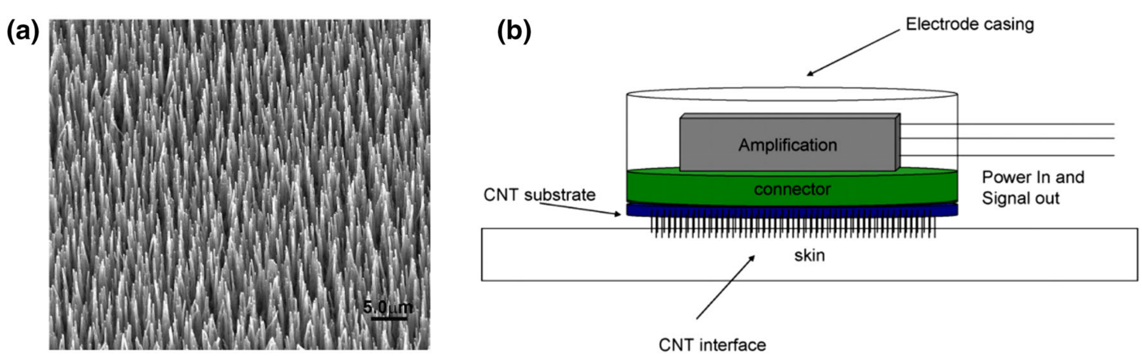

Fig. 6. Dry penetrating electrodes based on brush-like CNT arrays. (a) CVD-grown, multiwall CNT array. (b) Electrode prototype design: Brush-like CNT array barely penetrates the stratum corneum to provide a painless and stable electrical interface. Reproduced with permission.[70] Copyright 2008, Elsevier.

detection (Fig. 4f and g). Serpentine lines were used as the stretchable interconnects, and a DRL component was employed to reduce the noise. The intimate contact to the curvilinear surfaces of the skin reduces skin–electrode impedance and minimizes motion artifacts. The adhesion force tended to decrease with multiple attachments/detachments, but it can be mostly retained after a cleaning process. Electrode-to-skin impedance at 40 Hz was 241 kΩ for the CNT/aPDMS electrode as compared to 74.2 kΩ for the pregelled Ag/AgCl electrode. When subjected to motions with different frequencies, the root-mean-square (RMS) value of the motion artifacts was significantly smaller than that of metal thin films (as dry electrodes) for all motion frequencies, and it was slightly smaller than that of

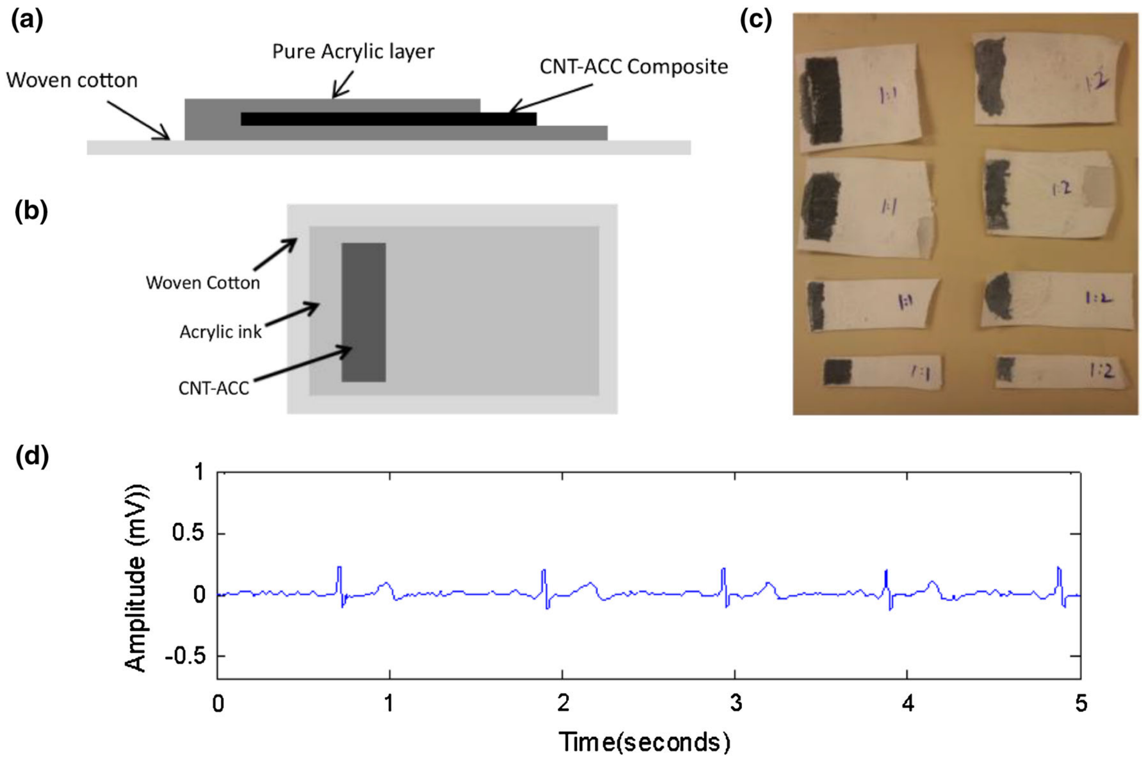

Fig. 7. Dry capacitive electrode based on screen-printed CNT–polymer composite. Schematic of the CNT–acrylic (CNT–ACC) electrode on woven cotton: (a) Cross-sectional view and (b) top view. (c) Actual screen-printed CNT–acrylic electrodes on woven cotton with difference sizes and two formulations of acrylic: CNT. (d) ECG signals obtained using a CNT–acrylic electrode with the formulation of 1:1 and size of 3 cm by 3 cm. Reproduced with permission.[72] Copyright 2012, Society of Photo Optical Instrumentation Engineers.

Ag/AgCl wet electrodes at 3 Hz, as illustrated in Fig. 4h. The human fibroblast cells cultured on the CNT/aPDMS and aPDMS surface highly proliferated, indicating low cytotoxicity (Fig. 4i). Figure 4j shows that no side effects were observed when wearing the electrode for one week and after removing the electrode from the skin. All the results demonstrated the feasibility of this thin, waterproof, self-adhesive, biocompatible CNT/aPDMS dry electrode for long-term wearable monitoring even under motion.

Besides CNT-polymer composites, ECG electrodes were also fabricated by coating a layer of conductive CNTs onto flexible and lightweight cotton fabric using tapioca starch paste as adhesive[64] and by directly patterned synthesis of vertical aligned CNTs with controlled spacing using a chemical vapor deposition (CVD) technique.[65] Low and stable impedance over time and comparable ECG signal quality to commercial wet electrodes were demonstrated.

Graphene, an atomically thin, two-dimensional arrangement of carbon atoms in a honeycomb lattice, has attracted significant attention due to its extraordinary properties, including high mechanical strength, good electrical and thermal conductivity, excellent chemical and thermal stability, and large specific surface area.[66,67] A simple and scalable dip-dry-reduce process was developed to coat conductive graphene onto fabrics (Fig. 5a and b), where nylon fabric was first dipped in a graphene oxide (GO) solution, and the GO was chemically reduced into reduced graphene oxide (rGO).[68] The graphene-clad conductive textile electrode had a conductivity of 4.5 S/cm, and it can withstand five cycles of washing. The electrode–skin impedance of the graphene-clad textile electrode ranged from 87.5 kΩ to 11.6 kΩ for frequencies swept from 10 Hz to 1 kHz, which was slightly larger than that of the commercial Ag/AgCl electrode (Fig. 5c). Both the ECG signals and the power spectral density (PSD) of the ECG signals from the graphene clad textile and commercial electrodes were highly correlated after filtering (Fig. 5d). Overall, the graphene-clad textile electrodes were reliable, durable, and comfortable, and the fabrication process was suitable for mass production.

Contact-Penetrating Electrode

In addition to noninvasive contact electrodes, CNTs have also been used for minimally invasive biopotential electrodes. Ruffini and coworkers employed a CVD-grown, multiwalled CNT forest as the penetrating ECG electrode, as shown in Fig. 6-a.[50,69–71] The brush-like structure, either coated or uncoated with silver, penetrated the outer layer of the skin (stratum corneum), increased the contact area of the CNTs and the skin, and circumvented the high impedance of the stratum corneum (Fig. 6b). The CNT array only pierced the stratum corneum with a penetrating depth of 10–15 μm to avoid the nerve cells and minimize the possible infection risk. Accordingly, a painless, low-noise, and low-impedance skin–electrode interface was achieved. Similar noise spectral densities were observed from both the CNT electrodes and the wet electrodes. Additionally, similar signal responses were obtained from both electrodes placed on pig skin.[69] Human trials confirmed the application of the CNT electrode for biopotential recording.[70]

Noncontact Capacitive Electrode

Although noncontact electrodes are easier to integrate with textiles, very few nanomaterial-based noncontact or capacitive dry ECG electrodes have been reported. A facile screen-printing method was adopted to print CNT–acrylic composite onto the woven using a screen mesh. A layer of insulating acrylic layer was also printed to encapsulate the conductive CNT composite, as shown in Fig. 7a and b.[72] Different sizes and CNT–polymer formulations of electrodes were prepared to investigate the effects of electrode size and CNT loading (Fig. 7c). It was found that a minimum electrode size was required to capture the signal, but a larger electrode size and higher CNT fraction increased the noise sensitivity. Electrodes with the size of 3 cm by 3 cm and CNT–acrylic volume ratio of 1:1 showed the best performance, as shown in Fig. 7d. The electrode was subjected to an extreme treatment to evaluate its skin biocompatibility. A total of 7.08 micrograms of CNTs was detected after an electrode sample with a CNT–acrylic volume ratio of 1:1 was immersed in ethanol/DI water solution and stirred for 12 h, indicating negligible CNTs were leached. Smart textiles such as smart vests based on CNT–acrylic composite can be readily developed for long-term wearable, unobtrusive health monitoring.

SUMMARY

Dry electrodes based on a variety of nanomaterials have been developed to overcome the limitations of commercial pregelled ones and to better satisfy the requirements for long-term, continuous, and even autonomous ECG monitoring. Although the dry electrodes demonstrated their robustness in ECG detection, pregelled ones still dominate the markets. We believe that more studies on scalable and low-cost fabrication methods for nanomaterial-based ECG electrodes, novel designs to achieve low electrode–skin impedance and stable electrode–skin interface, advanced integration/packaging techniques, progress on dry adhesives that can hold the dry electrodes securely in place without causing skin irritation,[9] and more understanding on the biocompatibility of nanomaterials with the human body and the environment will promote the development and application of dry biopotential electrodes. With the recent progress of other wearable components, such as sensors (e.g., motion sensors,[73] hydration sensors,[20] and glucose sensors[74]), wearable wireless transmission,[75] and wearable drug delivery devices,[76] an advanced wearable system combining long-term health monitoring and the illness treatment can be expected in the near future.

ACKNOWLEDGEMENT

This material is based on work supported by the National Science Foundation (NSF) through the ASSIST Engineering Research Center at NC State (EEC-1160483).

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