Abstract

The growing popularity of long-term, continuous, and unsupervised tracking of human physiological data for health care monitoring and preventive treatment has made biomedical applications of nanotechnology a major research focus. Generally, the monitoring and prevention of diseases in humans is performed through the collection of biomedical data and signals. In current methodologies, the transducers used to acquire human physiological data do not perform to the desired standard. For example, the silver (Ag) electrodes used to acquire electrocardiogram (ECG) data introduce distortion along with the information. In the proposed work, reduced graphene oxide (rGO) nanoparticles were prepared through chemical reduction and characterized using field-emission-scanning electron microscope (FE-SEM) and Raman analysis for biomedical applications. Subsequently, graphene nanoparticles-coated electrodes were fabricated and found to be suitable for obtaining human biomedical data for further analysis. A development board for ECG analysis was created, along with an android application, to monitor the performance of graphene nanoparticles coated electrodes in comparison to traditional electrodes. The comparison is performed in terms of the quality of the signal, the ratio of the signal to noise (SRN), and the impedance of the electrode to skin contact. Using Internet of Things (IoT), this monitoring can be done anytime and anywhere.

Keywords

Graphene nanoelectrode, Electrocardiogram analysis, Internet of Things, Impedance, Signal to noise ratio

Introduction

Nanoelectrodes play a central role in both electrochemistry research and bioelectrochemical analysis compared to the conventional electrodes. Due to their compact size, minimal noise, and rapid response, they are particularly well-suited for a wide range of applications [1-3]. Recently nanoelectrodes with dimensions less than 100 nm are a promising tool to know electrochemical processes at the nanoscale. Nanoelectrodes have been widely used to characterize nanoparticles, construct non-invasive electrochemical probes for the diagnosis because of their advantages [4]. Although the advances of nanoelectrodes are exciting and encouraging, the use of graphene-based materials for biomedical applications has a lot of challenges [5-7].

Although there are a variety of methods that are available to assess the electrode geometries at the nanoscale, almost none of the current techniques could have provide an extensive and real-time picture of the nanoelectrode during its measurements. Therefore, the fabrication and investigation of graphene nano-
electrodes for ECG live monitoring system using smartphone is described in this work. The paper describes the acquisition of ECG signal using a novel graphene-based electrode [8, 9]. The electrode proposed is fabricated by forming layers of graphene on the apex of a metallic layer of Ag/AgCl electrode using sputtering coating technique. First the methods of fabrication and their complications for graphene nanoelectrodes are highlighted. Then, the methods of characterization that are employed for the nanoelectrodes are emphasized [10]. Need for the advancement of nanoelectrodes is presented focusing on the properties of nanoelectrodes. Attention is also paid to the safety of graphene materials by analysing their long-term toxicity [11].

Seamless and real-time monitoring of the cardiac activities with the ECG plays a vital role in the treatment of cardiovascular diseases and conventionally the disposable gel type Ag/AgCl electrodes are employed which are simple and cost-effective during monitoring [12]. Due to the side effects like skin irritation and allergic reactions, these wet electrodes are not recommended for long term cardiac monitoring. Thus, the need for easy-to-use electrodes has led to the production of electrodes that eliminates the need for gel. It is found to be challenging to meet the stability in electrical characteristics between skin and the electrode for dry contact ECG electrodes [13]. To overcome the dry electrodes limitations, nanomaterial-based electrodes are used in prolonged ECG diagnosis due to the high electrical conductivity properties and flexibility [14, 15].

Materials and Method

Chemicals

All the chemical reagents used in this study, including potassium permanganate (KMnO₄), sodium nitrate (NaNO₃), hydrogen peroxide (H₂O₂), sulfuric acid (H₂SO₄) and graphite with 99% purity were procured from Sigma Aldrich, India Ltd. The reagents employed in the synthesis were of analytical grade and were utilized without any additional purification.

Synthesis of graphene nanoparticles

Graphene nanoparticles were synthesized using graphite as the parent material through a chemical reduction process. NaNO₃, nitric acid (HNO₃) was used as a precursor. 60 ml of HNO₃ was taken, and 20 g of graphite was added to it. Then HNO₃ solution was placed in a magnetic stirrer. Meanwhile 0.05 g of NaNO₃ has been added to the HNO₃ solution. Then, after obtaining a homogeneous black solution, 2 ml of distilled water was added drop by drop and constantly stirred for three to five days. Finally, the precipitated graphene nanoparticles were dried using heating mantle at 90 °C respectively and the dried graphene nanoparticles are powdered as shown in figure 1a and figure 1b.

Fabrication of graphene nanoparticles coated electrode

The motive of this project is to prove that the graphene nanoparticles coated electrodes are better than the commercially available Ag/AgCl electrodes for analysing patient’s cardiac reports. Ag/AgCl electrodes and graphene nanoelectrodes are shown in figure 2a and figure 2b. Sputter coating is a technique in which a functional coating is applied to a substrate through physical vapor deposition. The process begins by electrically charging a sputtering cathode, generating a plasma that results in the ejection of material from the target surface. The fabrication of graphene nanoparticles coated electrodes was done by sputtering coating technique to coat the graphene nanoparticles by physical vapor deposition on the commercially available Ag/AgCl electrodes as a thin film.

Characterization of graphene nanoparticles

The prepared nanoparticles are characterized by using FE-SEM and Raman spectral analysis and impedance analysis for rGO nanoparticles. These are the main characterization

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Figure 1: Graphene nanoparticles (a) Solution form and (b) Powdered form.

Figure 2: (a) Ag/AgCl electrodes and (b) rGO nanoelectrodes.
processes for the graphene nanoparticles to analyze the efficiency of the graphene nanoparticles coated ECG electrodes are best for patient cardiac diagnostic processes contrary to the commercially available Ag/AgCl ECG electrodes.

**Results and Discussion**

The prepared rGO nanoparticles and rGO nanoelectrode were synthesized as discussed in the method section. Then, these nanoparticles were physic chemically and electrical characterized using different instruments.

**Morphological (FE-SEM) analysis**

FE-SEM images are shown in figure 3a and figure 3b for rGO nanoparticles with 0.2 mole concentration. The surface morphology exhibits different surface variation on the rGO nanoparticles. Figure illustrates that uniformly aligned, fracture free and even surface of the ultra-thin sheet like arrangement, having a typical dimension of the particle is small (44 nm). The tiny particles have high surface area i.e., high surface to volume ratio. Thus, a larger number of atoms present on the surface of the particle when compared to inner atoms. These atoms which were present on the surface have free valence bonds (or dangling bonds) which makes them more active for absorption of other species or interacting with neighbouring surface atoms. The observed size of grain varied nearly in the range of 40 - 60 nm. The rGO nanoparticles showed better grain growth. The variation of grain size is in good accordance with mean crystalline size of all the nanoparticles.

**Raman spectral analysis**

Raman spectroscopy is a clear, effective, and non-destructive technique that uses a monochromatic excitation laser to confirm the material's structure. There are three interest peaks in the response in the graphene Raman spectroscopy. Figure 4 shows the distinctive Raman spectra for the in-plane vibrations of the conjugated π-bonds, which are 1347, 1586, and 2724 cm\(^{-1}\) for D, G, and 2D, respectively. When sp3 carbons are present in the basal carbon plane, as in disordered graphene and graphene oxide, the D peak can be utilized to identify flaws in graphene-based compounds. Monolayer graphene is characterized by the G and 2D band peaks, which typically occur at 1582 cm\(^{-1}\) and 2700 cm\(^{-1}\), respectively. The G band has a frequency that is approximately twice that of the D band, but second-order Raman spectra of graphene are reported to have a two-phonon band not having any kind of disorder or flaws. Although, if a structural change is made, the D, G, and 2D bands peaks might change because of the consecutive introduction of holes or sp3 centres in the graphene surface or basal plane, depending on the functionalization strategy chosen. This occurs because of flaws introduced into the carbon framework by the application of covalent bond-forming chemicals, which results in modifications to the vibrational excitation response that are quite different from those brought on by localized, physical flaws in sp2-conjugated carbon. The ID/IG ratio can also give a strong indication of the degree of disorder in the sp2 region as well as the existence of flaws, contaminants or chirality resulting from functionalization. This Raman spectra provides evidence of graphene nanoparticles. Based on the results it has been concluded that the graphene is the best suited for ECG electrodes [16].

**Electrical properties of rGO nanoparticles coated electrode**

Impedance measurement of skin–to-electrode contact has always been of interest due to the dependability of the collected biopotential. Skin conductivity may vary according to variations of conditions of either the stratum corneum or sweat proportions. To get a high-quality signal acquisition with negligible noise, the skin-to-electrode contact impedance measurement should be small and stable. The skin electrode contact impedance was measured by electrochemical impedance spectroscopy method [17]. Here, the electrode–to-skin contact impedance of the rGO nanoelectrode is measured against that of the conventional Ag/AgCl electrode. Figure 5 shows the values of impedance of conventional Ag/AgCl electrode ranges from 487 kΩ (at 10 Hz) to 17.3 kΩ (at 1 kHz), and the impedance of the rGO nanoelectrode varies from 356 kΩ (at 10 Hz) to 10.9 kΩ (at 1 kHz) [18, 19]. Figure 5 show that the rGO nanoelectrode has lower skin–electrode contact impedance compared to the
conventional Ag/AgCl electrode, resulting in less noise and a higher quality ECG signal [20]. Furthermore, performance of the electrodes is evaluated, and ECG signals were analyzed to calculate SNR using equation 1.

\[
SNR = 20 \log \left( \frac{S}{S' - S} \right)
\]  

(1)

Where \(S\) is the filtered ECG signal with a frequency ranging from 0.5 Hz to 100 Hz, and \(S'\) is defined as ECG signal without filtering. Before calculation, the power line interference (50 Hz) was removed from both signals [21, 22]. Table 1 summarizes the SNR of both Ag/AgCl electrode and rGO nanoelectrode.

**ECG live monitoring system**

**Hardware description**

The hardware setup for ECG live monitoring system consists of two circuits combined. One circuit (main circuit) is designed to gather all the necessary data from the patient and another one (transmitter circuit) is designed to transmit all the gathered data to the online cloud server to look over the data using the android application which is exclusively designed for proposed system. The main circuit contains ATMEGA328P microcontroller as it is easily programmable and reliable [23]. ESP8266-01 is used as the IoT transmitter module in the transmitter circuit. BMP180 sensor is used to get body temperature, MAX30100 sensor is used for blood oxygen saturation level and heartbeat rate and AD8232 module to get ECG graph of the patient. Above are the data to be obtained from the patient that can be live monitored through the android application using this proposed system and with the help of LCD display provided in the hardware operation [24].

**Software description**

An Android mobile application has been developed exclusively for the ECG live monitoring system. In figure 6, both the hardware setup and the android mobile application communicates by using the online cloud server where the patient data are transferred from the hardware setup to the android mobile application. This exclusive android mobile application is designed to show the raw data from the server in a representational manner. The body temperature, blood oxygen saturation level and heartbeat rate were represented in text format along with image representation and the ECG data is represented in graphical format [25].

**Output of the ECG analysis of prepared rGO nanoelectrode**

ECG signals were individually measured for graphene nanoelectrodes and conventional Ag/AgCl electrodes using three leads via ECG acquisition system for various scenarios shows in figure 7a to figure 7h. To obtain ECG signal, experimental testing of ECG electrodes on a 21-year-old male was performed to establish the ECG lead 1 configuration. Two active electrodes were placed on the left and right chest, while the driven right leg electrode was attached to the left waist for referencing [26, 27]. Two types of electrodes (graphene nanoelectrodes and conventional Ag/AgCl electrodes) were analyzed on a healthy 21-year-old subject were used in this work to analyze the acquired ECG signals in terms of the signal quality and skin-to-electrode contact impedance. The proposed graphene nanoelectrode demonstrates superior performance in acquiring ECG signals compared to the conventional Ag/AgCl electrode [28].

The signal quality and skin-to-electrode contact impedance of the graphene nanoelectrode were evaluated by impedance measurement. The results showed that the graphene nanoelectrode had a lower contact impedance and a higher SNR than the Ag/AgCl electrode [29]. This led to a more precise and clearer ECG waveform with less noise and more distinct PQRST features. The electrical activity of the heart during a cardiac cycle is reflected by the PQRST features on an ECG waveform, which are crucial for cardiac diagnosis. The PQRST node is where the P wave, QRS complex, and T wave converge on the ECG [30]. These waves correspond to different phases of cardiac depolarization and repolarization: the P wave shows the atrial depolarization, the QRS complex shows the ventricular depolarization, and the T wave shows the ventricular repolarization. By measuring the duration and

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**Table 1: SNR for electrodes.**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Electrode type</th>
<th>SNR (dB)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Ag/AgCl electrode</td>
<td>31.05</td>
</tr>
<tr>
<td>2</td>
<td>Graphene nanoelectrode</td>
<td>37.31</td>
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</table>
amplitude of these waves, the heart rate, rhythm, and conduction can be inferred. The graphene nanoelectrode offers a superior alternative to the conventional Ag/AgCl electrode for capturing these waves, as it has higher fidelity and resolution. This allows for a more precise diagnosis of cardiac conditions such as arrhythmias, ischemia, and infarction [31]. Hence, the graphene nanoelectrode offers a better performance in ECG measurement with its high SNR and low contact impedance. The impedance results varied from 487 kΩ (at 10 Hz) to 17.3 kΩ (at 1 kHz) for Ag/AgCl and from 356 kΩ (at 10 Hz) to 10.9 kΩ (at 1 kHz) for graphene coated electrodes [32].

Conclusion

In this paper, a novel graphene nanoelectrode was fabricated and its effectiveness was tested in terms of the signal quality and durability. The results from experimental testing clearly showed enhanced performance with graphene nanoelectrodes. The SNR has improved by 16.7%, greatly due to graphene coating. The signal shape has greatly improved with graphene nanoelectrodes than conventional Ag/AgCl electrodes. Thus, ECG signal had low-frequency fluctuation and high-frequency noise with graphene coated electrode. Impedance measurements of the ECG electrodes have shown reduced impedance due to the graphene coating compared to that of electrodes without coating which would increase the sensitivity of the electrode. Therefore, the graphene nanoelectrode reflects potential application in not only cardiac activity ECG monitoring systems, but also muscular (EMG) and neural activity (EEG).

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Conflict of Interest

None.

References


