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Facile and sorely conductive EDA electrode fabrication @ copper-graphene oxide context for fibromyalgia and myriad bio-medical diagnosis demand☆

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Abstract

Electrodes play a vital and huge role in the field of bio-medical. In order to eliminate the atmospheric corrosion of copper and silver which causes Red plague on the surface of electrode and to increase its efficiency for carrying microampere current signal from the human body to the processing unit, graphene oxide is synthesised with the copper. Due to its high conductivity and large surface area graphitized basal plane structure and the possibilities of mass manufacturing is available at low cost. Accordingly graphene oxide in solid state or in solution through Co-60, Pm-147, and Ti-204 have been investigated as catalyst support to design EDA (Electro Dermal Activity) electrode to diagnose fibromyalgia. All materials were synthesized by the method of chemical oxidation and graphite oxide exfoliation, and results were confirmed by characteristic analysis. The resultant structural and morphological properties were characterized by using X-ray diffraction (XRD), UV, FTIR (Fourier Transform Infrared Spectroscopy), Scanning Electron Microscopy (SEM). The XRD pattern clearly showed the formation of graphene oxide which was also confirmed by SEM images. An important aspect, its high conduction of micro signals travelling from the body to EDA/GSR (Galvanic Skin Response) instrument via resultant electrode is 13.8% more efficient than the existing electrodes like Cu/Ag/AgCl (Copper/Silver/Silver-chloride) which was confirmed by the variation in body resistance with respect to the voltage at constant current of 5 micro-amperes.

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Keywords: EDA, graphene, fibromyalgia, electrodes, GSR

1. Introduction

The ultimate goal of this study was to fabricate high end effective electrode by copper-graphene oxide synthesizing, which is more efficient and also to suppress the atmospheric corrosion of the electrode which cause red plague. This research particularly focused on EDA electrode design, directed towards diagnosing the fibromyalgia which is adversely affecting 70-90% of women [1]. Apart from fibromyalgia, Electrodes plays an important role in maximum medical diagnosis like ECG (Electro cardio gram), EEC (Electroencephalogram) and EMG (electromyogram). Now a day's high-definition electrode gels are used to increase the durability, skin safety and subjective pain [2]. Electro dermal activity (EDA) is the study of electrical property of the skin which holds the skin resistance which varies with the state of sweat glands in the autonomic nervous systems, which could be suitable for fibromyalgia diagnosis directly [1,3,4,5]. Fibromyalgia syndrome is manifested as chronic and diffuse musculoskeletal pain. In detail, an early diagnosis is possible between the ages of 29–37, but because of the patients null awareness it reaches 34–53 [1]. In present day, several types of materials are used to fabricate electrodes like Cu (Copper), Ag (Silver), AgCl (Silver-chloride), Al (Aluminum) are exhibits the property of carrying micro electrons. Among these materials, in this research graphene oxide was synthesized with copper because of their electrical, thermal, physical, and high conductivity. Graphene oxide can also ideal base for energy storage devices, sensors and transparent electrodes [6, 12]. At present, expensive noble metals such as Au, Ru, Pt are the best conducting materials for the oxygen reduction reaction. Among them, Pt named as noble metal as electro catalyst [13-26]. Since platinum is more costly, researchers identified the new metal salts called graphene oxide, which is perfect suit for highly conducting electrode design. The main objective of this research was to design an efficient electrode by the electrochemical reaction with copper-graphene oxide, which minimize the use of electrode gels and to reduce red plague on the surface of electrode due to atmospheric corrosion and to maximize the conductivity of electrons flow leads to proper micro-signals which provides high end solutions in the field of bio-medical.

2. Materials and Methods

2.1. Preparation of graphene oxide

GO was synthesized from graphite powder according to the modified Hummer's method. As an initial step, 2 g graphite powder was gradually added into a hot 60mL concentrated H_2SO_4 solution and stirred for 30 minutes. Further, 6 g of $KMnO_4$ was added pinch by pinch under stirring in order to avoid overheating and explosion and then it was left for another 150 minutes under stirring. Subsequently, 90 ml of distilled water was added drop by drop into the above mixture. After 15 minutes, 150 ml of distilled water and 5% of H_2O_2 were added in order to terminate the reaction. The product was washed with HCl (1:10) and then with water, and then suspended in distilled water. The brown dispersion was extensively dialyzed to remove residual metal ions and acids. After the unexploited graphite in the resulting mixture was removed by centrifugation, as-synthesized GO was dispersed into individual sheets in distilled water at a concentration of 0.47 mg/mL with the help of sonication, and further it was characterized with UV, FTIR, XRD and Scanning Electron Microscopy[27-31].

2.2. Preparation of Electrodes

In most researches Ag/Agcl (Silver/Silver-chloride) was used as signal sensing electrode. This research uses copper plate as an electrode with nano-coated graphene oxide. Copper is lesser in cost when compared to silver. This research provides sufficient data to prove the efficiency of copper electrode after electrochemical reaction with graphene oxide.

It is the very important to note that the working electrode considered as a critical variable in an electrochemical experiment. These working electrodes are where the reactions of interest take place and are usually made of an inert material. The potential of the working electrode is measured with respect to reference electrode. A typical reference electrode is a familiar saturated calomel electrode commonly used in pH measurement. By design, the reference electrode is always at a known potential. Since potential is a measurement with respect to the voltage difference between two points, the constant value of the reference electrode arising the working electrode potential. In electrochemical measuring setup, current flows in the solution between the working and the counter electrodes. The counter electrode is typically a wire constructed of copper or other inert material. The below Fig1, shows the reaction setup

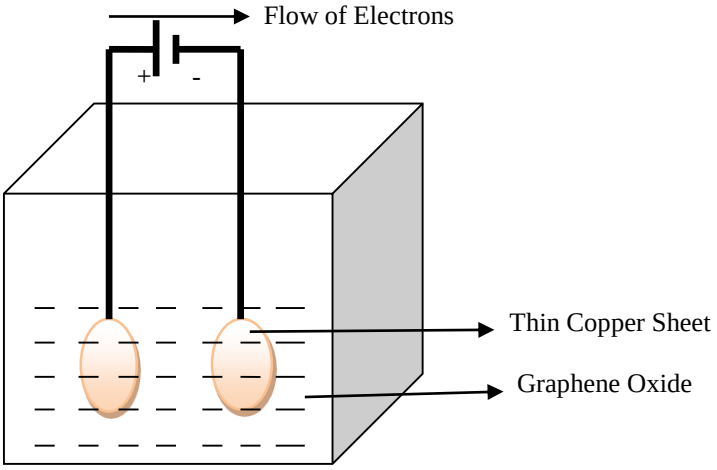


Fig. 1. Electrochemical Experimental Setup

2.3. Characterization

The FT-IR spectra were obtained on a Fourier Transform Infrared spectrometer (EQUINOX 55, Bruker, Germany). The samples for FT-IR measurement were prepared by grinding the dried powder of reduced graphene oxide. The grain size and surface morphology were observed by the field emission scanning electron microscope (FESEM). FESEM images of the Graphene Oxide (GO) have well defined and interlinked three-dimensional Graphene sheets, forming a porous network that resembles a loose sponge like structure. X-ray diffraction, XRD, data were collected using a Rigaku D2000 Bragg-B0.rentano diffractometer, equipped with a copper rotating anode, diffracted beam monochromator tuned to radiation, and a scintillation detector. The entire data were collected using reflection modeαCu K geometry. In health-care electrodes plays an important role to detect chronic stress related problem affecting different health related diseases like fibromyalgia, including cardiovascular diseases and cerebrovascular diseases [32]. Considering the major role of electrodes among bio-medical research field, this research developed an efficient copper coated graphene oxide electrode which suppresses the usage of conventional Cu/Ag/AgCl (Copper/Silver/Silver-chloride) electrodes. Efficiency of electro dermal activity can be measured with the help of GSR (Galvanic Skin Response) circuit in terms of graphical representation with respect to voltage and body resistance [33].

3. Results and discussions

The synthesized GO by Hummer's and Modified Hummer's methods are characterized by UV, X-Ray Diffraction Analysis (XRD), Fourier Transform- Infrared Spectroscopy (FT-IR), Field Emission Scanning Electron Microscopy (FESEM) [34-37].

3.1. Graphite oxide-UV Characterization

Figure2 depicts the ultraviolet-visible spectra of reduced graphene oxide and the spectrum of graphene oxide has an absorption peak at 260 nm which is shifted to 300 nm in graphene. This is a red shift which is due to the electronic

configuration in graphene in the reduction of graphene oxide. The absorption peak at 260 nm is attributed to transition of aromatic C–C ring. The UV spectra of reduced grapheme oxide on the other hand show the red shift at 260 nm. This absorption peak is attributed to n-π transition of C–O bonds now embedded by exfoliation and intercalation on the graphene oxide.

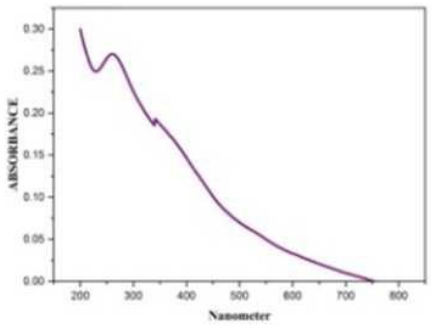


Fig. 2. UV Characterization of GO

3.2. Graphene oxide -FTIR Characterization

An FTIR spectrum analysis includes in graph was performed to investigate the structure and functional groups of the materials, of graphene oxide and its reduced form are depicted in Figure 3. The GO showed apparent adsorption bands for the carboxylC=O (1755.31 cm−1), aromatic C=C (1385.09 cm−1), epoxy C–O (1086 cm−1), alkoxy C–O (1045 cm−1), and hydroxy –OH (3300.03 cm−1) groups. The presentation of oxygen-containing functional groups, such as C=O and C–O, further confirmed that the graphite indeed was oxidized into GO and was consistent with the literatures [36, 38-40]. The presentation of C=C groups showed that even graphite had been oxidized into GO; the main structure of layer graphite was still retained. The result of FT-IR synthesis both further demonstrated the successful synthesis of GO.

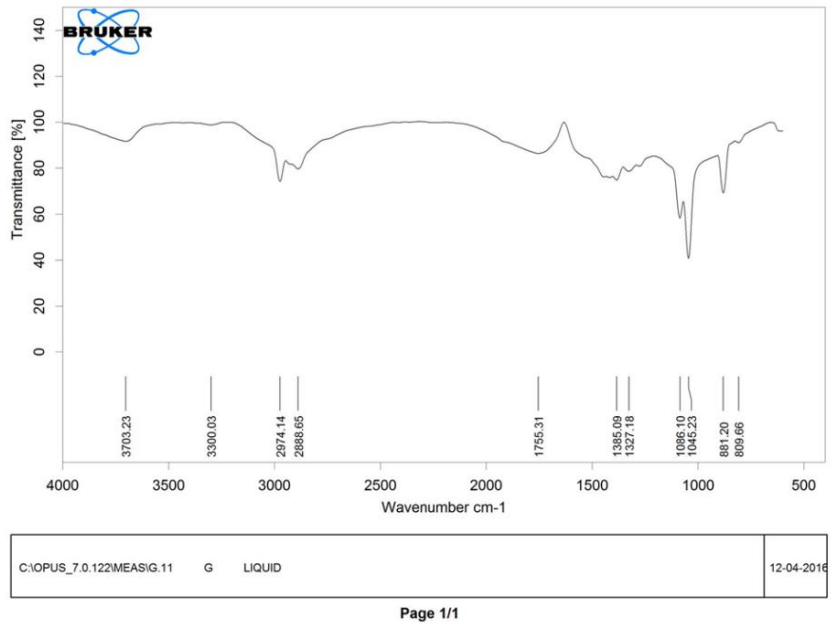


Fig. 3. FTIR Characterization of GO

3.3. - FESEM Images

Figure 4 depicts the FE-SEM images of the obtained GO flakes, with a film thickness of about 4μm. Figure 5 shows the FE-SEM image of graphene coated on copper. The GO material that constitutes randomly aggregated, thin, crumpled sheets closely associated with each other to forms a disordered solid [39].

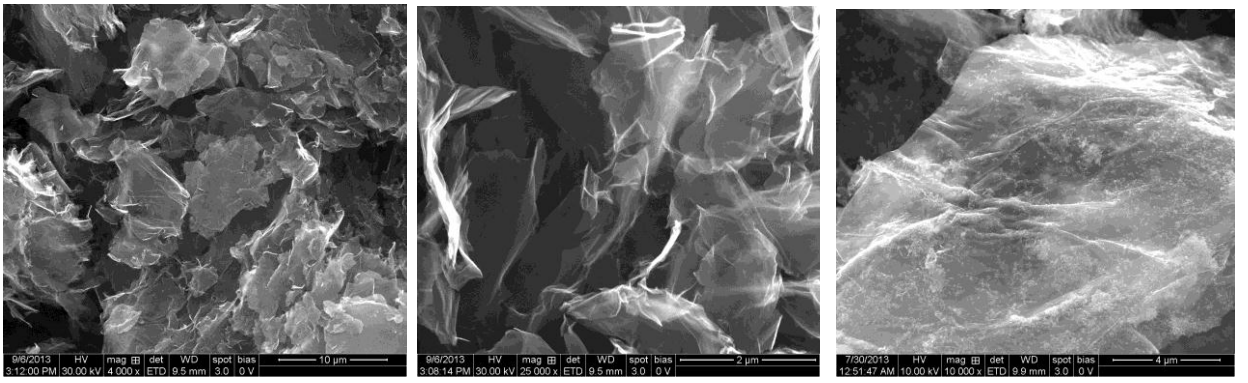


Fig. 4.Plain Graphene oxide

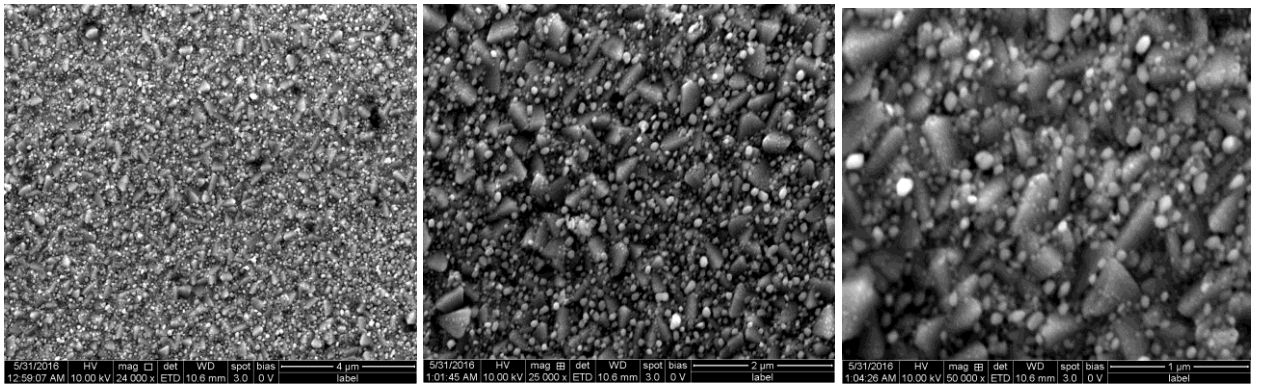


Fig. 5. Graphene oxide coated on Cu.

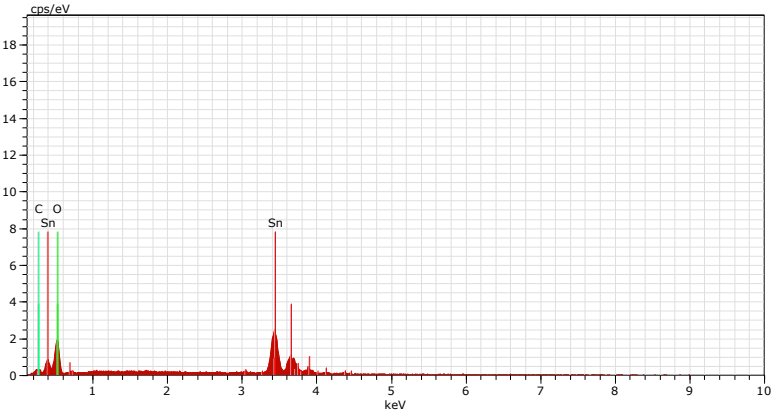


Fig. 6. Spectrum: Acquisition for EDAX

Table1. Spectrum: Acquisition for EDAX

E1 AN [WL%]	Series [WL%]	Unn. [at.%]	C norm. [WL%]	C Atom.	C Error (1 Sigma)
Sn 50	L-series	75.13	76.39	30.04	2.72
O 8	K-series	22.25	22.52	65.69	4.15
C 6	K-series	1.08	1.10	4.27	0.52
Total		93.36	100.00	100.00	

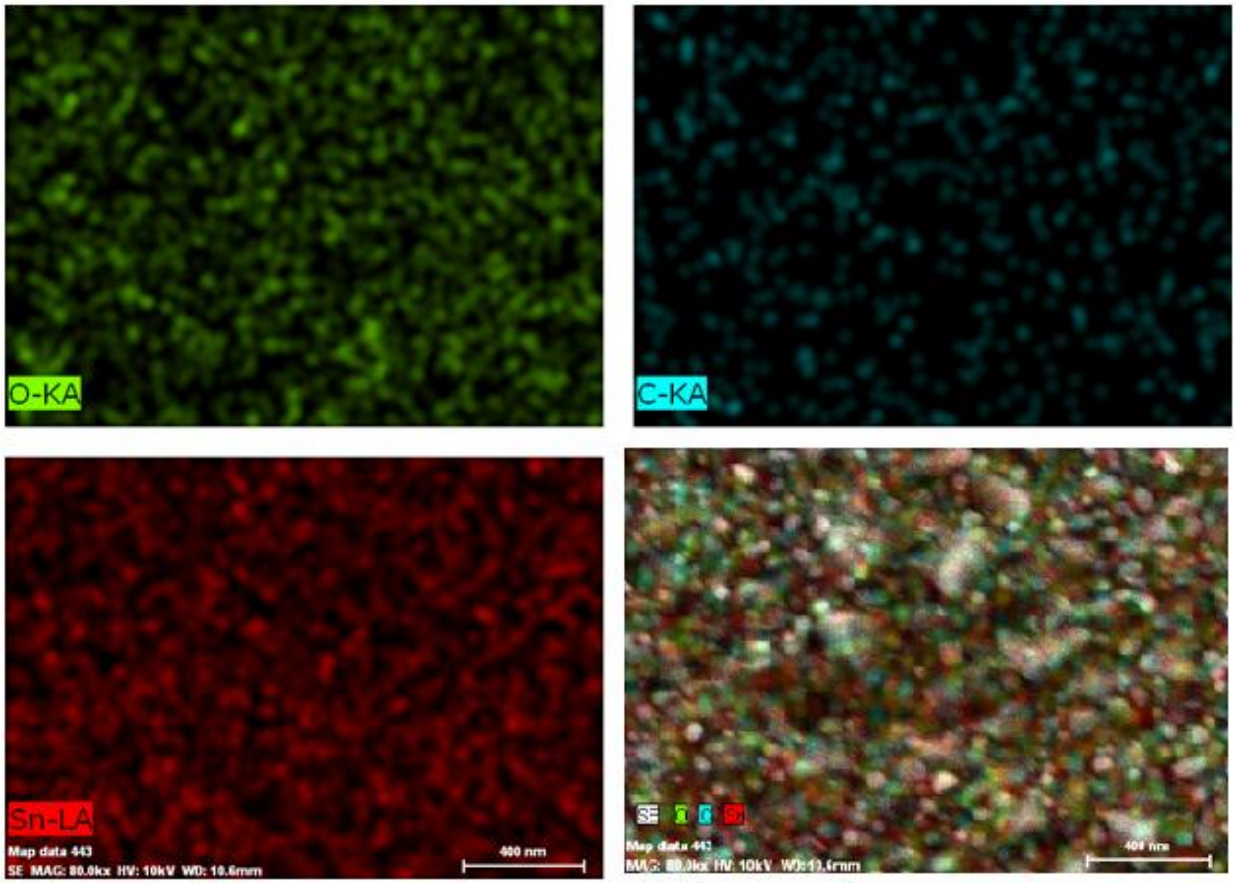


Fig. 7. Spectrum Acquisition for EDAX

In the EDAX pattern of GO fig 6 & from the table 1, three peaks strong and sharp peak at Sn^{50} is 76.39%, O^{8} is 22.52% and C^{8} is 1.10%. This EDAX result are related to the exfoliation and reduction processes of GO and the processes of removing intercalated water molecules and the oxide groups.

3.4. XRD Pattern

In the XRD pattern of GO fig 8, two peaks strong and sharp peak at $2\theta = 11.7^{o}$ corresponds to an interlayer distance of 7.6 Å (d002). Graphene oxide shows a broad peak that can be fitted by using a Lorentz function into three peaks centered at $2\theta = 20.17^{o}$, $23,78^{o}$ and 25.88^{o}, corresponding to interlayer distances of 4.47, 3.82 and 3.53Å, respectively. This XRD result are related to the exfoliation and reduction processes of GO and the processes of removing intercalated water molecules and the oxide groups.

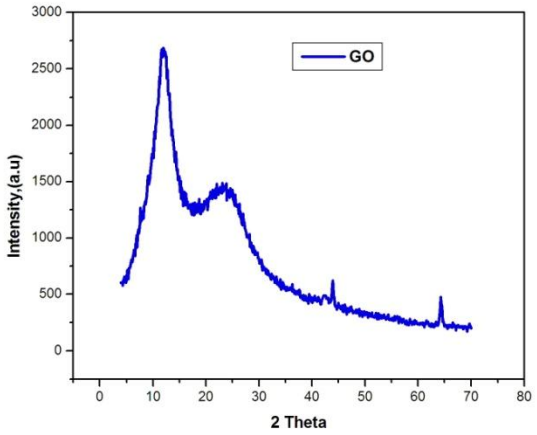


Fig. 8. XRD Pattern

3.5. Graphical representation of voltage with respect to body resistance

Synthesis of graphene oxide with small piece of copper plate can be proved with the help of FESEM. Likewise in order to prove the electrode efficiency, the body resistance can be measured with respect to voltage at constant current [41]. The circuit diagram is given in Fig9 (a) [41].

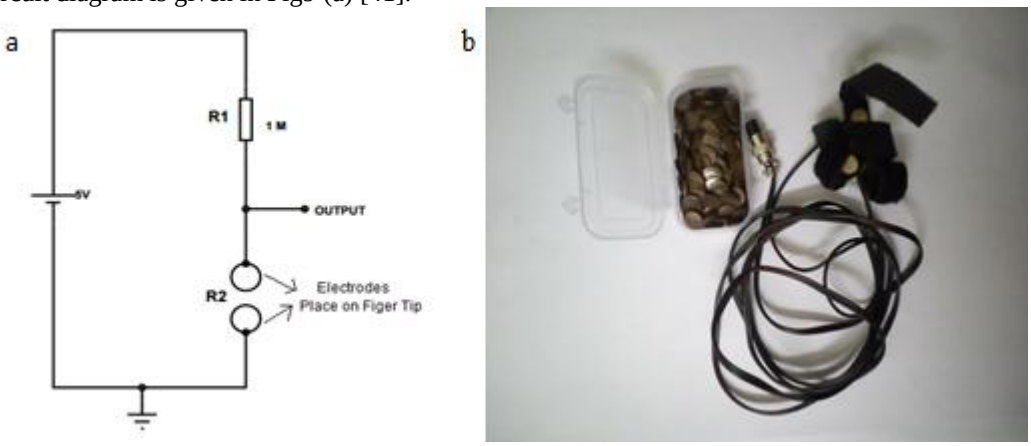
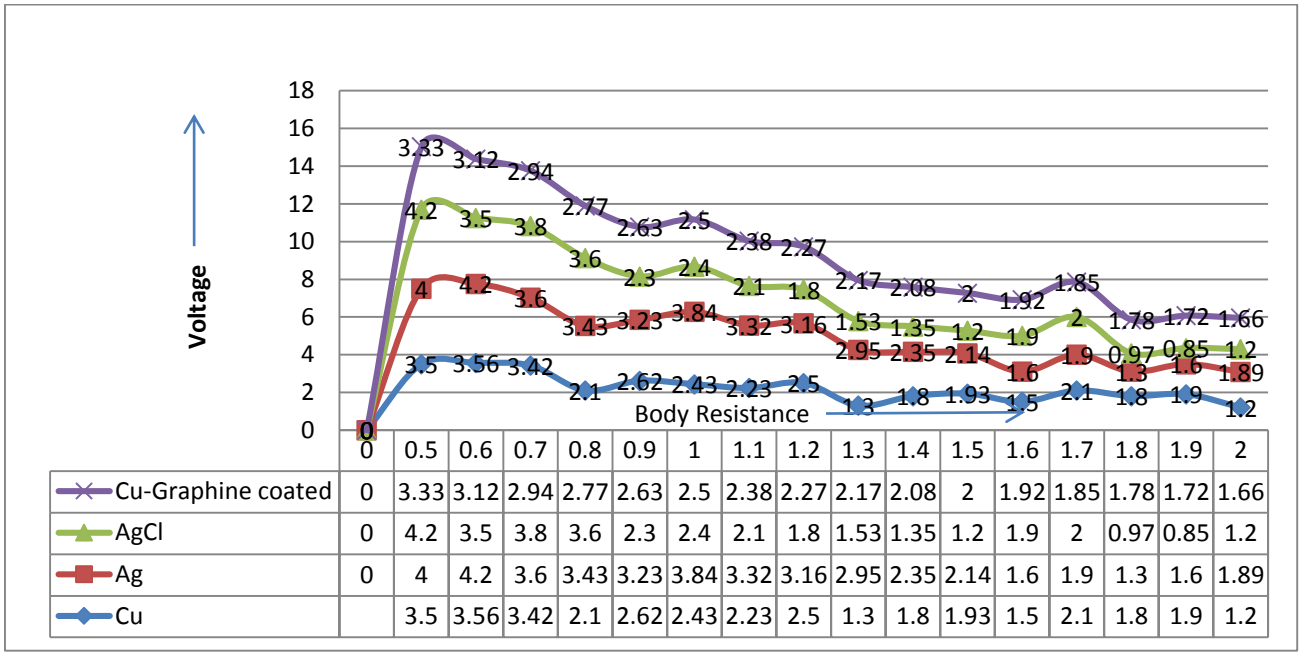


Fig.9. (a) EDA Basic measuring circuit; (b) Copper Electrode Pieces with Probe.

Every 10-50 microsecond sweet gland in ANS (Autonomous Nervous System) induces sweet depends on subject's emotion. Thus we can identify the state of mind with the help of proper electrodes as shown in Fig 9(b). In Fig 9(a), R1 is constant resistance which never changes during signal acquisition. R2 is the body resistance of the subject which continuously varies depends on the state of mind. Using R1 and R2, the circuit measures the output voltage of the subject with the help of voltage-divider formula I.e.

$$V_{out} = (R2/R1+R2)\, V_{in} \quad (1)$$

Figure 10, shows the clear variation of electro dermal activity, using nano-coated copper-graphene electrode via graphical representation which is recorded using agilent DSO (Digital Storage Oscilloscope) which can be cross check with the voltage divider formula as shown in equation 1.



	0	0.5	0.6	0.7	0.8	0.9	1	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2
Cu-Graphine coated	0	3.33	3.12	2.94	2.77	2.63	2.5	2.38	2.27	2.17	2.08	2	1.92	1.85	1.78	1.72	1.66
AgCl	0	4.2	3.5	3.8	3.6	2.3	2.4	2.1	1.8	1.53	1.35	1.2	1.9	2	0.97	0.85	1.2
Ag	0	4	4.2	3.6	3.43	3.23	3.84	3.32	3.16	2.95	2.35	2.14	1.6	1.9	1.3	1.6	1.89
Cu		3.5	3.56	3.42	2.1	2.62	2.43	2.23	2.5	1.3	1.8	1.93	1.5	2.1	1.8	1.9	1.2

Fig. 10. Graphical representation of Voltage vs. Body resistance at constant current(5µA)

Table2. Body resistance Versus Voltage at constant 5µA current

Resistance (Meg Ohm)	Cu(V)	Ag(V)	AgCl(V)	Cu-Graphene coated(V)	Time (min)
0		0	0	0	t_0
0.5	3.5	4	4.2	3.33	t_1
0.6	3.56	4.2	3.5	3.12	t_2
0.7	3.42	3.6	3.8	2.94	t_3
0.8	2.1	3.43	3.6	2.77	t_4
0.9	2.62	3.23	2.3	2.63	t_5
1	2.43	3.84	2.4	2.5	t_6
1.1	2.23	3.32	2.1	2.38	t_7
1.2	2.5	3.16	1.8	2.27	t_8
1.3	1.3	2.95	1.53	2.17	t_9
1.4	1.8	2.35	1.35	2.08	t_{10}
1.5	1.93	2.14	1.2	2	t_{11}
1.6	1.5	1.6	1.9	1.92	t_{12}
1.7	2.1	1.9	2	1.85	t_{13}
1.8	1.8	1.3	0.97	1.78	t_{14}
1.9	1.9	1.6	0.85	1.72	t_{15}
2	1.2	1.89	1.2	1.66	t_{16}

Above figure 10, shows the variation in body resistance with respect to voltage at constant current of 5 microamperes for 16 different time intervals t_o-t_{16} with the delay time of 1 minute. In this only graphene coated copper electrode

provides more efficient variation in body resistance with respect to voltage as per the EDA reaction. The voltage and resistance in copper-graphene electrode is indirectly proportional to each other, which shows the efficiency of electrode. In case of cu/Ag/AgCl electrodes, it's clearly shows there is an improper variations among body resistance and voltage between the time periods of t_0-t_{16}.

5. Conclusion

Modified Hummers method has been synthesized and utilized to prominent high area graphene oxide. This method was carried out with the highest conversion level of graphite flakes to graphene oxide and shows that pure graphene oxide is formed. XRD patter confirms the presence of graphene oxide to hexagonal structure. The particle sizes formed in copper were in the range of 4μm to 10 μm from FESEM and EDAX. FTIR confirms the formation of graphene oxide on thin copper plate. The comparison of body resistance with respect to voltage from t_0-t_{16} for various materials like Cu/Ag/AgCl/Copper-graphene was studied. Among them copper-graphene electrode is more efficient due to its indirect proportionality of voltage-resistance from t_0-t_{16} and t_{16}-t_0. Simultaneously the usage of electrode gels and red plague of atmospheric corrosion has been reduced.

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