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Impedance Based Vitamin D Measurement Sensor and Algorithm for Human Wellness

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Abstract: While entering the modern society, medical technology has been able to cure almost all kinds of diseases. However, autoimmune diseases are increasing rapidly due to environment, food, and indoor life. In particular, vitamin D is lacking in about 90 % of Koreans. As a result of this, many middle-aged and older women are taking calcium, but most of them do not know their vitamin D levels. Based on this background, the goal of this paper is to develop a vitamin D measurement technique using a quantum analyzer that is capable of measuring various kinds of vitamins and minerals, and to prepare a plan to easily measure vitamin D by attaching it to a UVB device that is currently used in the hospital. The quantum analyzer was designed based on the impedance principle, and the impedance change according to vitamin D concentration was able to confirm a significant proportional relationship between vitamin D and impedance. In addition, the correlation between vitamin D and impedance was confirmed by in vitro experiment using lab mice, and the measurement error of the impedance meter for vitamin D concentration in the blood was confirmed to be about 12.7 %.

Keywords: Portable sensor, Data processing, Vitamin sensor, Impedance sensor.

1. Introduction

1.1. Vitamin D Status of the People

According to the Korea Centers for Disease Control and Prevention, when based on the 30 ng / ml in vitamin D level, 91.3 % of female and 95.0 % of males in Korean adults are vitamin D deficient. The average vitamin D level in urban women in Korea is 15 ng / ml, which is the highest vitamin D deficiency in the world. If the latitude is more than 35 degrees north, the shortage of vitamin D increases significantly in autumn and winter.

It is harmful to the human body when vitamin D is deficient, or excessive administration of vitamin D is done to the human body. Because Vitamin D is stored in the body fat due to its fat-soluble properties, toxic symptoms may occur. In addition, vitamin D, beyond safe quantities, can cause elevated uptake of calcium and phosphorus. It also can cause hypercalcemia, hyperphosphatemia and hypercalciuria due to increased bone resorption in the skeleton, In addition, some side effects such as gastrointestinal symptoms, neuromuscular symptoms, and thirst may occur.

Therefore, it is necessary to take the proper amount of vitamin D by auto synthesis.

However, in most cases, vitamin D levels in the body are unknown. Many women who are postmenopausal take in Ca to prevent their osteoporosis. But, they don't know the level of vitamin D, the mediator of Ca absorption.

The measurement of Vitamin D levels is optional in periodic test that is covered by National Health service, so people who want to know their own vitamin D levels have to pay the additional cost of the test. In addition to osteoporosis, vitamin D level related diseases are directly linked to immunity that is the underlying cause of modern chronic diseases such as cancer and allergic diseases, and the incidence of vitamin D related diseases continues to increase.

Therefore, it is essential to develop a vitamin D level diagnostic device that will help to absorb an adequate amount of vitamin D.

1.2. The Process of Ultraviolet B Making Vitamin D

The process that ultraviolet ray B makes vitamin D is as follows: 7-dihydrocholesterol, the cholesterol metabolite, is produced during digestion after eating food. Ultraviolet B then breaks the 7-dihydrocholesterol molecule ring in the skin and is synthesized as vitamin D3 (Cholecalciferol).

Liver Vitamin D3 goes to the liver through the blood stream, then converts to a 25-vitamin D by combining with enzyme (Half-life 3 weeks).

25-vitamin D, which circulates in the kidney blood, goes to the kidneys and turns into active vitamin D (Half-life 4 to 6 hours). Fig. 1 shows the example.

1.3. Existing Vitamin D Measurement Principle

Since Vitamin D is converted to a metabolite called 25 (OH) D in the body and is present in the blood, in the existing vitamin D measurement method, the concentration of 25 (OH) D is measured and is used as the concentration of vitamin D. The notation 25 (OH) D means that (OH) is bound to the 25^{th} carbon of vitamin D. For example, a blood level of 30 ng / mL means that 30 mg of vitamin D is contained in 1 mL(cc) of blood.

Therefore, in order to measure this, a visit to the hospital is necessary to conduct blood concentration test through blood sampling.

1.3.1. Existing Vitamin D Measuring Devices

Existing vitamin D measuring devices -Vitastiq

The principle of "EAV (bio current measurement) Test" developed by Dr. Reinhard Voll from Germany in the 1940s, which is a test that measures the current of each meridian in the body to determine its health status, is applied to the products. The EVA (electroacupuncture According to Voll) system considers the cell as a single ion battery and analyzes the characteristics of meridian reaction by external weak current stimulation.

If you touch the meridian with the pen-like vitastiq that corresponds to the elements you want to know, you can check the nutritional status of your body without a blood test.

Existing Vitamin D measuring device - How to use Cue Health Tracker ?

This device measures the amount of Vitamin D by collecting the samples of blood or body fluids with a product stick and placed in a cue box.

Existing Vitamin D measuring device -Smartphone devices that measure vitamin D levels

This is a smartphone device developed by researchers at Cornell University and measures the cholesterol and vitamin D levels. It looks similar to a credit card reader attached to a smartphone. This device attaches to a smartphone camera and measures the user's cholesterol and vitamin D levels in two minutes with a drop of blood. To use this device, the user drops a blood sample onto a test strip that is woven with chemicals designed to react in a particular way, then take picture of a test strip with the smartphone. This device processes blood samples that respond to test strips, determines the levels of cholesterol or vitamin D from the images, and displays the results on a smartphone display. This technology also works on saliva or sweat, and tells the users their cholesterol or vitamin D levels.

Although various vitamin D measuring devices are presently available, most of them have a problem that human blood or body fluids to be taken for the measurement of vitamin D. In addition, the sample sticks and strips for collecting blood or body fluids are usually for one-time use, so it is inconvenient to take care of them.

To complement these shortcomings, this paper developed vitamin D measurement technology using an application of impedance principle based quantum analyzer. It is convenient to use compared to existing measurement methods, since it measures only impedance without collecting body fluids or blood. It also has the advantage of reducing the inconvenience of users who want to measure vitamin D without using the sample sticks or strips.

2. Method

2.1. Development of Vitamin D Measuring Device

Development of vitamin D and calcium measuring device using quantum analyzer

We have developed a device that selectively displays signals that measure only vitamin D and calcium. We developed the display that can calibrates the measurement using vitamin D and calcium, and can displays them with numerical value. A quantum analyzer is a device that can measure various metabolic functions in the body.



Fig. 1. Example of using a quantum analyzer.

• Development of simulation board for analysis

We designed and made a simulation board that can analyze and measure micro-current of human body by receiving signal from a sensor module.

It is designed to use external and internal power modes and LCD display is used as a display window (option). The User Controller is designed as a simple key shape for easy operation. In addition, it is made to be easily handled by making the board small as shown in Fig. 2.



Fig. 2. Example of Simulation Board.

• Application Development

The development of the device operating program for analysis and measurement of the output waveform from the sensor is to set the way of displaying measurement and to analyze the energy waveform of the sensor module.

A CPU with an A/D converter built-in is selected, and the standard value for sensor is selected as well. The program that supports C compiler, macro assembler, real-time OS, simulator, etc. was developed. In addition, the LCD display is configured to display the letters, numbers, etc. on the screen to show the operation status and debugging is possible without an external ROM / RAM.

2.2. Principle of Measurement Separation Signal and Quantitative Analysis of Vitamin D

Introduction of vitamin D measurement technique using the impedance measurement principle

The bioelectrical impedance measurement assumes that the living body is a homogenous tubular conductor, and it is used to calculate body water and body fat using a formula where capacity is proportional to the square of the height divided by the impedance. However, because in vivo impedance is not a homogeneous tubular conductor according to the assumption above, impedance and various variables may exist.

The bioelectrical impedance analysis (BIA) method has the advantage of being easy to use for patients regardless of age and gender by meeting the two conditions of precision and practicality of measurement, and it also has simplicity that does not require special techniques for measurement [5-7]. The bioelectrical impedance (BIA) is the method that utilizes the difference in electrical conductivity depending on the biological characteristics of the tissue and predicts the body composition. In this method, electrical conductivity is proportional to the amount of water and electrolytes, and decreases as the shape of the cells becomes closer to the circle, and is affected by moisture, muscle, and fat content.

2.3. Development of a Vitamin D Measurement Sensor Module

Development of an Impedance-based Quantum Analyzer Module

Many quantum analyzers are known to use the principle of impedance and analyze human body by measuring electrical in vivo. In this paper, we use an impedance meter to predict the concentration of vitamin D in vivo. When sending a minute alternating current signal to a living body, electricity flows along highly conductive water, and the impedance of body water, fat, muscle, etc. are different from each other depending on the water content. Fig. 3. shows the example of sensor.



Fig. 3. Vitamin D measurement kit. Vitamin D measurement sensor module applying impedance measurement principle.

In this study, the impedance meter is developed in order to check the correlation between vitamin D and impedance. The impedance meter is consisted of two electrodes and a measuring instrument body and is designed to set the step according to the measurement intensity.

Impedance changes caused by vitamin D

In order to check the change in impedance due to vitamin D, we measured impedance using diluted solution of vitamin D concentration. As a result of confirming the impedance measurement value using vitamin D, we found that the impedance increased in a concentration-dependent manner. However, the difference in impedance according to the concentration of vitamin D was not found to be significant. This indicates that, in a practical application, there is not a large gap between the titration and the over or under-titration of vitamin D in vivo, thus indicating that there is difficulty getting an accurate measurement. Fig. 4. Shows the results.

Table 1. Impedance change according to vitamin D concentration (Unit: Ω , Concentration: ng/mL).

Vitamin D conc.	0	0.005	0.048	0.244	0.716	2.79	10.1	50.6	250
1	2.136	2.036	2.215	2.436	2.831	3.125	3.564	4.256	4.825
2	2.015	1.953	2.135	2.485	2.653	3.245	3.617	3.983	4.596
3	2.165	2.046	2.184	2.645	2.536	3.358	3.661	4.126	4.548
Average	2.105	2.012	2.178	2.522	2.673	3.243	3.614	4.122	4.656
SD	0,080	0.051	0.040	0.109	0.149	0.117	0.049	0.137	0.148



3. In Vitro Experiment

3.1. Estimation of Vitamin D by Impedance Measurement Using Animal Model

The mouse used in the experiment

- It is C57BL. C57BL/6 or C57Black66 (C57 black 6) is an inbred mouse strain for research, and the model is mainly used for the cause and analysis of human genetic diseases. It is the most commonly used mouse strain because it is a similar-genotype mouse, easily reproduced, and sturdy.

\circ Impedance measurement in animal model

- Impedance is measured using a C57BL/6 mouse (male, 8 weeks old). Impedance was supplemented by connecting a copper wire to the electrode to enable measurements on the back of the mouse. The measurements were performed three times for each individual. No conditions specific to vitamin D were administered, and impedance was measured in a normal mouse.

- After measuring the impedance, the blood of the mouse was collected and the amount of vitamin D in the blood was measured. Fig. 5 and Fig. 6 shows the experimental procedures and results.



Fig. 5. Measurement of Mouse Impedance Using Impedance Measuring device.

Table 2. Impedance in mouse skin.

Impe-	Mouse							
dance (Ω)	1	2	3	4	5	6		
1	2.518	2.431	2.24	2.313	2.46	2.382		
2	2.501	2.357	2.255	2.328	2.445	2.387		
3	2.524	2.372	2.229	2.269	2.343	2.401		
4	2.513	2.328	2.269	2.284	2.328	2.387		
5	2.521	2.313	2.255	2.269	2.372	2.416		
Ave- rage	2.5154	2.3602	2.2496	2.2926	2.3896	2.3946		
SD	0.00901 7	0.04589 9	0.01542	0.02672 6	0.05979 4	0.01390 3		



Fig. 6. Impedance measurement on mouse skin.

3.2. ELISA Analysis According to the Vitamin D Concentration

Vitamin D measurement using the kit

The amount of vitamin D was measured using the Vitamin D measurement kit (Enzo, ADI-900-215), 25(OH) Vitamin D ELISA kit. Fig. 7 shows the results



Fig. 7. Vitamin D standard measurement using vitamin D assay kit.

Vitamin D measurement in mouse blood

- After confirming the skin measurement value, the blood of the mouse was collected and the plasma was separated. The collected blood was kept in a refrigerated state, and after about 1 hour, the blood was centrifuged at 2000 rpm for 10 minutes. Then, the

plasma of the upper layer was separated and used for vitamin D analysis.

Relationship between Impedance and Blood Vitamin D

Through in vitro experiments, we confirmed the correlation between mouse impedance analysis value and vitamin D measurement. Fig. 8 and 9 shows the results.

Experimental results show that the relationship between impedance and blood vitamin is proportional to a certain proportion. However, further study is needed to apply animal experimental measurements directly to humans in significance. From the result of this research, it is difficult to determine the exact amount of vitamin D with the vitamin D measurement method using impedance. However, if the range of vitamin D to impedance is set, it is possible to judge whether the vitamin level is deficient, normal or excessive. However, when applied to a human, it is necessary to reset the data of the relevant experiment. Impedance basically measures the electrical resistance, and measurement of the impedance using the living human body is influenced by various factors. Especially, the effect on the fat seems to be great, and it is thought that it will affect not only the measurement of the Vitamin D but also various kinds of bio-phenomena measurements using the impedance. Measurement of vitamin D using impedance seems to be correlated and more detailed study is needed.

Ontial Dansity	Mouse							
Optical Density	1	2	3	4	5	6		
1	0.264	0.223	0.284	0.249	0.246	0.238		
2	0.245	0.264	0.296	0.258	0.244	0.238		
3	0.251	0.236	0.248	0.236	0.234	0.253		
4	0.213	0.269	0.234	0.275	0.258	0.237		
5	0.212	0.246	0.246	0.261	0.237	0.241		
O. D. Average	0.237	0.2476	0.2616	0.2558	0.2438	0.2414		
O. D. SD	0.023399	0.019165	0.02681	0.014481	0.009338	0.006656		
Vitamin D Conc. (pg/mL)	28166.99	25312.6	22131.18	23376.68	26286.91	26929.7		
SD (pg/mL)	2780.892	1959.281	2268.145	1323.371	1006.849	742,4994		

Table 3. Measurement of vitamin D in mouse blood using ELISA kit.





Fig. 9. Comparison of mouse impedance value and vitamin D value in the blood.

The measurement error of the impedance meter to the concentration of vitamin D in the blood is the sum of the mouse measurement impedance error (2.5 %)and the maximum value of the vitamin D measurement error (10.2 %) in the blood, and there was an error of about 12.7 %. The correlation between the Impedance measured in the mouse and the impedance in the blood was verified. The formula for measuring vitamin D in the blood using impedance was Y = 23624X-30550 (Y: predictive value of vitamin D in blood (pg/mL), X: impedance value), and predicted vitamin D in the blood with this formula. Fig. 10. Shows the results.



Fig. 10. Correlation check between Impedance and vitamin D.

3.3. Test Result

We made the Impedance-based vitamin D analyzer, one of the principles of the quantum analyzer, and performed in vitro experiments. In this experiment, the impedance analysis by vitamin D concentration verified change in amount of the impedance depending on the concentration. The similarity of the impedance measurement and the pattern in the mouse skin was also verified as a result of measuring the amount of vitamin D in the mouse blood of mice using an ELISA-based vitamin D kit.

Impedance-based vitamin D measurements were patterned depending on the concentration in the blood, but there was a difference in accuracy. Measurement of vitamin D using impedance has been difficult to get precise quantification due to the variation of values depending on various environmental factors (such as Body composition, fat, protein ratio, etc.). However, it seems that patterns of the concentration are similar, so it is possible to predict the deficiency, normal, and excess levels of vitamin D.

The measurement error of the impedance meter for the vitamin D concentration of vitamin D in the blood was confirmed to be about 12.7 %. (Measurement error = maximum value of mouse measurement impedance error + maximum value of vitamin D measurement error in blood). The predicted value of vitamin D in blood using impedance measured in mouse was predicted by the formula Y = 23624X-30550 (Y: predicted value of vitamin D in blood (pg/mL), X: impedance value).

4. Conclusions

To reduce the incidence rate of vitamin D related diseases, we have developed a vitamin D diagnostic device that will help to absorb adequate amounts of vitamin D. We also developed vitamin D measurement techniques using the impedance principle based quantum analyzer by complementing the disadvantages of existing vitamin D measuring devices.

To measure the amount of vitamin D in the body, we developed a vitamin D measuring device using a quantum analyzer, a simulation board for analysis, and an application, and introduced a vitamin D measuring method using the impedance measurement principle.

We also developed a vitamin D measurement sensor module and an impedance-based quantum analyzer module and measured the impedance changes caused by vitamin. Through this process, we could confirm a significant correlation between the vitamin D concentration and the impedance.

After verifying the correlation between the vitamin concentration and the impedance, an in vitro experiment using an animal model was conducted. In this experiment, the amount of change in impedance depending on the vitamin D concentration was confirmed. The result of measuring the amount of vitamin D in the blood of the mouse using an ELISAbased vitamin D kit verified the similarity of patterns. However, additional research is needed to apply animal test measurements directly to humans in significance.

The measurement error of the impedance meter for the vitamin D concentration of vitamin D in the blood was confirmed to be about 12.7 %. (Measurement error = maximum value of mouse measurement impedance error + maximum value of vitamin D measurement error in blood). The predicted value of vitamin D in blood using impedance measured in mouse was predicted by the formula Y = 23624X-30550 (Y: predicted value of vitamin D in blood (pg / mL), X: impedance value).

This study showed that the measurement method of vitamin D using impedance has a difficulty to determine precise amount of vitamin D. However, we think that it is possible to judge the vitamin deficiencynormal-excessiveness when the range of vitamin D to impedance is set.

When we use the vitamin D measurement device using the impedance-based quantitative analyzer developed in this research, it is possible to check the amount of vitamin D in an individual's body, so that it can help to absorb an appropriate amount of vitamin D by blocking vitamin D deficiency and excess. In particular, it can help female osteoporosis patients after their menopause to control the absorption of vitamin D which acts as a mediator of calcium absorption, and is expected to provide new information on disease prevention and treatment technologies. It is expected that the impedance-based quantum analyzer principle will be used to analyze various body components in the future.

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Fabrication of Novel Amperometric Sensor for the Detection of Zinc Metal as an Environment Pollutant

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Abstract: Outstanding conductivity and biocompatibility of Carbon nanotube (CNT) and conducting polymer (CP) have shown the unparalleled superiorities in the area of electrochemical sensors. Emphasis has been given on the types of functionalization, fabrication of sensor, role of graphite, CNT and CP in environment monitoring and assay strategies. It is very important to develop a simple, effective, sensible, reliable and accurate method to detect heavy metals present in the environment as a pollutant. Other traditional or conventional methods like Atomic Absorption Spectrophotometer, Flame Photometer, Gravimetery etc. have their own limitations and disadvantages. We have fabricated novel graphite, CNT and CP (polyaniline) based amperometric sensor for the detection of Zinc metal as an environment pollutant. The electrochemical performance of amperometric sensor was tested by Cyclic Voltammetry, Ampereometry and Linear Sweep Voltammetry experiments. The developed amperometric sensor displays good electrochemical activity towards the detection of Zinc present in the environment activity towards the detection of Zinc present in the environment. Storage and stability conditions were also tested.

Keywords: Amperometric Sensor, Conducting polymer, Electrochemical biosensor, Environmental pollutant, Zinc.

1. Introduction

The detection of metals as an environment pollutant proves to be very beneficial for mankind because like the other pollutants such as pesticides, household chemicals, the harmful metals represent a growing environment pollutant concern [1-2]. Environment contamination by the trace and toxic metals shows a major environmental pollution issue, which ended in an increasing demand for the sensitive and selective sensor [3]. Harmful metals that come out from the anthropogenic activities present in environment which is several times greater than the limits of necessary intake in the living beings [4]. The harmful metals get accumulated in the environment and enter in the food chain of living beings which create a health risk for the living beings. Hence, early, easy and quick detection of harmful metals present in

the environment becomes very important [5-6]. If the harmful metals are taken up by the living organism by the ingestion or inhalation they cause the nausea, vomiting and diarrhea [7-8]. The harmful metals also responsible for the long – term disease like cancer and damage to the central nervous system [9-10]. Fig. 1 shows impact of Zinc metal on the life of human beings if taken in excess.

There is several analytical methods available for the detection of metals like inductively coupled plasma with mass spectrometry, Atomic absorption spectrophotometer, flame photometer, gravimetric and stripping voltammetry. All these methods have their own limitations and are time – consuming and convoluted. To overcome these limitations, there is urgent need to fabricate amperometric sensor which is a rapid technique, provide the accurate information, portable and cost effective analytical method [11]. For a definitive electrochemical biosensor there is need of a suitable receptor in the recognition layer, the receptor is a molecule that binds the marked object [12-17]. In the last few decades, there has been reported many applications of conducting polymers [18-20]. Conducting polymers cast a strong and penetrable surface this behave as a transducer to convert the chemical interaction between the receptor and target analyte into an electric signal [21-24]. Due to its flexible nature and high order of conductivity, conducting polymer could be grafted on the surface of any conducting and non-conducting support [25-27].

Fig. 1. Impact of Zinc metal on the life of human being if taken in excess amount.

In continuation to our earlier study [28-31], in this paper, we have focused on the fabrication of graphite, carbon nanotube and conducting polymer based electrochemical sensor for the detection of Zinc metal as an environment pollutant.

2. Experimental

2.1. Synthesis of Conducting Polymer Polyaniline

5.0 M of aniline is dissolved in the 1.0 M solution of the protonic acid. The temperature was maintained between 1.0 to 4.0 $^{\circ}$ C. The oxidant (FeCl₃) which is precooled is added drop wise to the ice-cold acidic solution of aniline. After sometime the colour of the polyaniline turns to dark green. The solution was continuously stirred for about 6.0 hours. The precipitate was washed with dilute HCl and then with the acetone and dried in vacuum oven maintained at constant temperature of 80.0 $^{\circ}$ C for 24.0 hours. It is notice that productivity of the polyaniline decreases after 5.0 hours hence in order to complete polymerization reaction, reaction time was increased to 8.0 hours.

2.2. Preparation of the Working Electrode

The carbon paste electrode was prepared by thoroughly mixing of graphene, Polyvinyl pyrrolidone (PVP), carbon nanotube (CNT), conducting polymer (polyaniline), paraffin and potassium ferrricynide and was homogenized in an agate mortar using a pestle to obtain the paste. The paste was then packed tightly into the glass electrode in order to avoid entrapping of air in to the matrix. A copper wire then inserted externally in order to establish electrical connection with the electrochemical workstation. For every reading, the outer surface of the electrode having copper wire was renewed by polishing with the emery paper. The cyclic voltammetric experiments were carried out by using $Fe(CN)_6^{3-}$ as an electrochemical probe. Phosphate buffer solution was prepared by using sodium chloride, Potassium chloride, disodium phosphate, Potassium dihydrogen phosphate and double distilled water. The prepared electrode was rinsed several times with the sodium acetate buffer solution. For every reading, the surface of electrode was renewed by removing some amount of paste. The working electrode was stored at 4.0 °C in dark place. Fig. 2 shows schematic diagram of conducting polymer modified graphite polarizable electrode.

Fig. 2. Schematic diagram showing working of conducting polymer modified graphite polarizable electrode.

3. Results and Discussion

3.1. Characterization of the Polyaniline

The synthesized polyaniline was characterized by UV-visible, Fourier transform infrared (FT-IR) spectroscopy and X-ray diffraction (XRD) spectroscopic techniques.

3.1.1. UV-visible Spectra of the Polyaniline

The absorption spectra of the polyanilines is may be due to multiple distribution of the quinoid and benzenoid ring along the polyaniline backbones, different substituents, different products resulted from possible side reactions, cyclization, conformation effects and reduction in ring symmetry [32]. Fig. 3 shows the UV-Visible spectra of polyaniline as a function of wavelength. The UV-Visible absorption spectra shows band at 329 nm.

Fig. 3. UV-Visible absorption spectra of polyaniline.

3.1.2. FT-IR Spectroscopy of Polyaniline

FT- IR studies have been carried out for the characterization of the polymeric film using FT-IR spectrometer having the resolution in the range 450-4000 cm⁻¹. FT-IR absorption spectra of the polyaniline is shown in Fig. 4. The bands related to N-H stretching of an aromatic amine (N-H) appears in the region of 3691.7 cm⁻¹ and this is attributed to the free N-H stretching vibrations. The bands of the – NH₂ group assigned to the asymmetric and symmetric stretching. The bands corresponding to C=N and C=C for the quinonoid and the benzanoid unit occurs at the 1600 and 1579 cm⁻¹. The fingerprint region of the polyaniline appears 466.77 cm⁻¹ to the 420.48 cm⁻¹.

Fig. 4. FTIR spectra of polyaniline.

3.1.3. XRD Analysis

X-ray diffraction pattern of PANI is shown in Fig. 5. The peak around 25° is the characteristic of π conjugation in PANI. PANI is only partially crystalline with conducting metallic islands separated by large amorphous regions as evident from the XRD spectrum. The diffraction peak of the PANI occurs between the 10 to 40 degree due to the parallel and the perpendicular periodicity of the polymer [33]. There is the presence of benzenoid and the quinoid rings in the PANI chain makes the low crystalline nature of the conducting polymer [34]. The XRD pattern of the poly-aniline shows a broad peak at $2\theta = 37.8$ degree which shows the amorphous nature of PANI in its emeraldine salt form [35]. The interplanar distance and crystalline size are estimated by Braggs law and

Debye-Scherer equation [36]. During the oxidation of the aniline monomer the presence of initial acidic medium highly affects the crystallization which increases metallic character in the poly-aniline [37]. Fig. 5 shows X-ray diffraction pattern of conducting polymer poly-aniline.

3.1.4. TEM Analysis

The needle-shaped or nano-web structures are seen in TEM image of polyaniline (Fig. 6). It is reported that the organic precursor of aniline can be converted into electronically conductive carbon through pyrolysis processes at high temperatures [38]. In this process of synthesis of polyaniline, probably carbons are produced from the oxidation process of aniline, which may increase the conductivity of polyaniline. Average particle size of polyaniline was observed to be 30.0 nm.

All the electrochemical measurements were performed using a Palmsens electrochemical interface, Netherland.

Fig. 5. X-ray diffraction pattern of conducting polymer polyaniline.

Fig. 6. TEM image of conducting polymer polyaniline (PANI).

3.2. Cyclic Voltammetry for the Detection of Zinc Metal in the Environment

The cyclic voltammetry experiments were performed to detect Zinc metal with the help of specially designed and fabricated conducting polymer, CNT and graphite based working electrode. Platinum wire was used as auxiliary electrode and Ag, AgCl/KCl_{sat} as a reference electrode. The electrode surface was preliminary treated by polishing, degreasing with alcohol and ultrasonic cleaning. The analyte (hydrazine) displays a reversible CV which is observed when all the initial analyte can be recovered after a forward and reverse scan cycle. The CV was performed with the help of conducting polymer, CNT and Graphite powder modified electrode in the PBS solution containing Zinc. We observed a large peak – shaped Zinc oxidation current at 2.3 A at a potential of 1.14 V.

Fig. 7. Cyclic voltammogram resulting of reversible reduction and oxidation of 1.0 mM Zinc at a bare electrode from spectrally pure graphite, carbon nanotube and Polyaniline based amperometric sensor at a pH of 6.5 at room temperature and scan rate of 0.01 Vs^{-1} in the phosphate buffer solution (PBS).

3.3. Linear Sweep Voltametric Experiment for the Detection of Zinc

Linear sweep voltammetric experiments were performed in order to study the electrochemical behavior of the working electrode [39-40]. It is observed from the linear sweep experiments (Fig. 8) that value of current increases continuously up to 0.17 V and then starts decreasing up to 0.6 V. Value of limiting anodic peak current I_{pa} was found to 3.8 A for 1.0 mM of Zinc.

Fig. 8. Linear Sweep voltammetry experiment carried out for Zinc metal showing anodic peak current I_{pa} whose intensity depends upon concentration of Zinc metal.

3.4. Amperometric Detection of Zinc

Amperometry experiments were performed at fixed potential i.e. OCP against Ag, AgCl/KCl_{sat} as a reference electrode. Variation of current (mA) with time (s) was investigated at constant potential. It is observed from the amperometric experiments (Fig. 9) that the value of current first decreases and then becomes constant. The fabricated amperometric sensor shows that response current decreases linearly between 2.0 to 0.15 mA with time. It is observed that in the absence of zinc, there is no anodic and cathodic oxidative and reductive current peak [41]. This behavior shows a strong and irreversible adsorption of the analyte on the surface of the electrode.

Fig. 9. Amperometric study showing variation of the current with respect to time.

3.5. Selectivity, Reproducibility and Storage Stability

The selectivity of CP-CNT-GCE towards zinc under the optimum condition was studied for a number of potential interferents. The good reproducibility and excellent storage stability gave an opportunity to CP/CNT/GCE as promising electrocatalyst for electrochemical techniques determination of Zinc. For this the electrodes were stored at refrigerated condition 4.0 °C and used periodically for the analysis of zinc at an interval of five days. The sensor response of electrode was fairly stable even after 40 days of storage.

4. Conclusions

Fabricated non enzymatic Graphite, CNT and conducting polymer based amperometric sensor was tested for its electrochemical performance for detecting environment pollutants. The integration of graphite, carbon nanotube and conducting polymer into this amperometric sensor brings new strategies for enhancing their electrochemical performance. The electrochemical performance of the electrode was tested by Cyclic Voltammetry, Ampereometry and Linear Sweep Voltammetry experiments. Value of limiting anodic peak current I_{pa} was found to 3.8 A for 1.0 mM of Zinc. A large peak – shaped Zinc oxidation current was found to be 2.3 A at a potential of 1.14 V. Selectivity, reproducibility and storage stability of the electrode was also tested for 40 days. The method was successfully used for the precise, sensitive, selective, easy and fast electrochemical technique for determination of Zinc metal as an environment pollutant.

Fig. 10. Effect of storage time on the response of working electrode based amperometric sensor in 0.1 M sodium phosphate buffer, pH 7.0 at a temperature of 4.0 °C. Standard assay conditions were used for each assay.

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Determination of Trace Amount of Cadmium(II) in Environmental Samples by Functionalized Graphene Oxide Modified Carbon Paste Electrode

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Abstract: In this study graphene oxide was functionalized by 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) and incorporated into a carbon paste electrode. This modified electrode was applied for determination of trace amount of cadmium (II). The analysis procedure is consist of three steps, firstly, an open circuit accumulation in stirred sample solution was occurred for 7 min. Cd^{2+} was accumulated on the surface of a modified Carbon paste electrode via forming Cd-5-Br-PADAP complex. This step was followed by medium exchange to a 0.1 mol L⁻¹ HCl solution, where the accumulated cadmium was reduced for 15 s at -1.10 V (vs. Ag/AgCl). Finally, cadmium was oxidized, and voltammograms were recorded by scanning the potential in a positive direction. The calibration plot was linear over the cadmium concentration range from 0.25-210 µg L⁻¹. The detection limit was 9.7×10^{-2} µg L⁻¹. Using this new modified carbon paste electrode, trace level of Cd²⁺ in water samples was determined.

Keywords: Carbon paste electrode, Cadmium, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol, Graphene oxide, Water samples.

1. Introduction

The presence of elements like lead, cadmium, arsenic, mercury and chromium, even at low concentrations (<2 ppb) is highly undesirable due to their toxicity [1]. Cadmium is highly toxic to certain organs of both humans and animals, including nervous, immune, reproductive, and gastrointestinal systems [1–3]. Ingestion of any significant amount of Cd^{2+} causes immediate poisoning as well as damage to the liver and the kidneys because of their tendency to accumulate in the body, toxicity, and low clearance rate [4]. So, determination of trace level of Cd^{2+} in water samples plays an important role in the environmental pollution monitoring due to the cumulative toxicity of Cd^{2+} .

Several analytical approaches have been applied for the determination of trace amounts of cadmium in biochemical and environmental resources, such as, spectrophotometry [5], flame atomic absorption spectrometry (FAAS) [6], graphite furnace atomic absorption spectrometry (GFAAS) [7], inductively coupled plasma atomic emission spectrometry (ICP-AES) [8] and electrochemical methods [9-10]. However, owing to the ponderous and sophisticated instrumentation the spectroscopy methods are fairly cumbersome and not suitable for the in situ measurements.

On the contrary, the electrochemical techniques are interesting methods for trace analysis of heavy metals. These methods are characterized by high sensitivity, good selectivity, simplicity, low cost and easy data read-out [11-13]. Thus, various electrochemical methods, equipped with different modified electrodes have been reported for the determination of Cd(II). Among all the electrochemical methods, voltammetric methods provide more powerful tools for the determination of cadmium ions [14-15].

A simple way to confine electronically insulating materials on an electrode surface, and to further exploit their properties in electrochemistry, was achieved by dispersing them into a conductive carbonbased composite, like carbon paste.

Carbon pastes are well known as useful materials for the fabrication of various electrometric sensors for analytical purposes [16-18]. The operation mechanism of modified carbon paste electrodes depends on the properties of the modifier materials used to import selectivity towards the target species. Because of the advantages such as stable response and easy renewal of surface, considerable attention has been given to the preparation of modified carbon paste electrodes.

Graphene which is a single layer of carbon atoms closely packed into honeycomb two-dimensional (2D) lattice, has recently received a lot of attention. The fascinating properties of graphene such as high mechanical stiffness [19], extraordinary electronic transport [20] and excellent antibacterial activity [21] would pave the way for future carbon-based device architectures. Graphene can be produced via different approaches such as mechanical exfoliation of bulk graphite, epitaxial chemical vapor deposition on substrates and chemical vapor deposition which starts from carbon precursors.

Recently, Graphenes have aroused extensive interests in electrochemistry field due to its super conductivity, high surface area, and wide potential window [22].

The aim of this work is to develop a simple, selective and sensitive method for determination of Cd^{2+} by using functionalized graphene oxide modified carbon paste electrode. Graphene oxide can be easily functionalized with a modifier in order to change its selectivity toward a specific ion. In the present study, graphene oxide was functionalized by 5-Br-PADAP which led to the development of a stripping voltammetric method for the determination of Cd^{2+} with a wide linear range, good reproducibility and low detection limit. So, the procedure was applied for determination of Cd^{2+} in water Samples.

2. Experimental

2.1. Reagents and Solutions

Graphene oxide was synthesized by Modified Hammer method [23]. The stock solution of 1000.0 mg L^{-1} Cd²⁺ was prepared by dissolving 2.744 g Cd(NO₃)₂ 4H₂O in doubly distilled water. The accumulation solution for cadmium was bicarbonate buffer (pH 9.5). High purity nitrogen was used for deaeration. The other chemicals such as 5-Br-PADAP

(Fig. 1) were purchased from Merck Company. A 0.05 % solution of 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol was prepared in ethanol. Doubly distilled water was used for all experiments. Graphite powder, Paraffin oil and all other reagents were of analytical grade from Merck or Sigma without further purification.

Fig. 1. The structure of 5-Br-PADAP as an anion/chelator.

2.2. Instrumentation

Voltammetric experiments were performed using a Metrohm electroanalyzer (Model 757 VA computrace). The measurements were recorded using VA computrace version 2.0 on windows 98 functional system. All voltammograms were recorded with a three-electrode system consisting of an Ag/AgCl reference electrode, a platinum wire as the counter electrode, and modified carbon paste electrode as the working electrode. A Metrohm 710 pH meter was used for pH adjustments.

2.3. Preparation of Graphene Oxide

Modified Hummers' method was used to prepare Graphene oxide (GO) sheets. In the current synthesis, 5.0 g of graphite powder and 2.5 g sodium nitrate were mixed with 80 mL sulfuric acid in an ice bath for 2 h. Then, 12.0 g of potassium manganate was added under stirring. The mixture was kept at 36 °C for 1 h, then diluted with 160 mL distilled water, and further 560 mL warm water was added and the temperature was kept at 98 °C for another 2 h. After that, for reducing the residual potassium manganate 10 mL of hydrogen peroxide was added to the mixture. The mixture was stirred for 2 h until turned yellow. Finally, graphite oxide powders were obtained by centrifuging the mixture. The powders were washed with diluted HCl to clean out any remains of salt, and then re-dispersed in ultra pure water and centrifuged. The obtained powder was finally dried under vacuum. The graphite oxide powder was exfoliated into GO monolayer sheets by sonication for 2 h after dispersion in distilled water [23].

2.4. Preparation of 5-Br-PADAP Functionalized GO

For synthesis of 5-Br-PADAP functionalized GO, 1.0 g of GO was suspended in 50 mL of an aqueous solution containing 1.0×10^{-3} mol L⁻¹ 5-Br PADAP. The solid was shaken until the supernatant solution

became practically colorless. The modified solid was carefully washed with doubly distilled water several times to remove the occluded materials. Then the solid was oven dried at 350 K for 12 h.

2.5. Preparation of Modified Carbon Paste Electrode

By thoroughly mixing an accurate amount of 65 % graphite powder, 23 % paraffin and 12 % modified GO (W/W) the carbon paste electrode was prepared. Then, the paste was inserted and compressed firmly in the cavity of the bottom of the glass tube with internal diameter 5 mm and a height of 3 cm. The surface of all electrodes was renewed by replacing the old surface with the new carbon paste. The surface of modified carbon past electrode was smoothed on a piece of soft paper. A copper wire which was inserted into a glass tube from the other side, established an electrical connection.

2.6. General Procedure

differential anodic For pulse stripping voltammetric experiments, the modified carbon paste electrode was immersed in a 20 ml of bicarbonate buffer solution (pH 9.5) containing a known amount of Cd²⁺ and the solution was stirred for 7 min. This was followed by medium exchange to a 0.1 mol L⁻¹ HCl solution, where the accumulated cadmium was reduced for 15 s at -1.1 V. Finally the differential pulse voltammograms were recorded from -1 to -0.5 V (with 25 mVs⁻¹ scan rate, 100 mV pulse amplitude, and 4 ms pulse period. The cadmium peak was absorbed at -0.78.

2.7. Principle of Method

Based on the above observations and under the optimum conditions of the experiments, the possible pathways for the analysis cycle, from the modification of GO to the stripping voltammetry, are postulated below:

Modification of GO with 5-Br-PADAP:

$$GO+5-Br-PADAP_{(sol)} \rightarrow [5-Br-PADAP/GO]$$
 (1)

Accumulation step via complex formation:

$$\frac{\text{Cd}^{2+}_{(\text{sol})} + 5\text{-Br-PADAP/ GO}_{(\text{sur})} \rightarrow}{[\text{Cd/5-Br-PADAP/ GO}]_{(\text{sur})}}$$
(2)

Reduction step at -1.1 V:

$$\frac{[Cd/5-Br-PADAP/GO]_{(sur)} + 2e^{-} \rightarrow}{Cd^{0}_{(sur)} + [5-Br-PADAP/GO]_{(sur)}}$$
(3)

Stripping step via positive scan (from -1 to -0.5 V):

$$Cd^{0}_{(sur)} \rightarrow Cd^{2+}_{(sol)} + 2e \tag{4}$$

3. Results and Discussion

3.1. Physicochemical Characterization of Graphene Oxide

In this study, SEM was used to investigate the structure and morphology of GO nanosheets. As it can be seen in SEM image (Fig. 2), GO nanosheets are formed by the exfoliation and restacking processes.

Fig. 2. Scanning electron microscopy micrographs for graphene oxide.

Also FTIR was used to represent the functionalized groups on GO surface that were formed by oxidation process. The bands related to C-O (ν (epoxy or alkoxy)), O- H (ν (carboxyl)) and O-H (broad coupling ν (hydroxyl)) were seen in their proper places (Fig. 3).

Fig. 3. FTIR spectra of graphene oxide.

3.2. Voltammetric Behavior of Cadmium on the Modified Electrode

The behavior of the Cd^{2+} at 5-Br-PADAP-GO/CPE was studied by differential pulse voltammetry between -1 to -0.5 V versus an Ag/AgCl reference electrode. Fig. 4(a) shows a typical differential pulse voltammogram obtained for the 5-Br-PADAP-

GO/CPE in bicarbonate buffer solution (pH 9.5). In the absence of Cd^{2+} in the solution, no well-defined voltammetric wave attributable to the oxidation of bicarbonate buffer or 5-Br-PADAP was observed within the applied potential window.

Fig. 4(b) indicates a differential pulse voltammogram obtained for the unmodified CPE in bicarbonate buffer solution containing $15 \ \mu g \ L^{-1}$ cadmium ions. Also, this figure shows a very small anodic peak which is related to oxidation of cadmium.

The differential pulse voltammogram for the Cd^{2+} at GO modified CPE is shown in Fig. 4(c); one small anodic peak at -0.78 was observed that can be related to oxidation of Cd^{0} to Cd^{2+} . When 5-Br-PADAP-GO/CPE was immersed into the solution including cadmium ions, a high increase in the peak current of the oxidation of cadmium was seen (Fig. 4(d). Comparing these figures demonstrated that the modified CPE has the ability to determine cadmium at low concentrations with high sensitivity.

Fig. 4. DP voltammograms of: (a) Unmodified CPE electrode in 15.0 μ g L⁻¹ Cd²⁺ in medium (b) 5-Br-PADAP/CPE whit no Cd²⁺ in the medium, (c) GO/CPE in 15.0 μ g L⁻¹ Cd²⁺ in medium (d) 5-Br-PADAP-GO/CPE, with 15.0 μ g L⁻¹ Cd²⁺ in the medium. Conditions: stripping medium: 0.1 mol L⁻¹ HCl solution, accumulation solution: bicarbonate buffer (pH 9.5), reduction potential = -1.10 V, reduction time = 15 s, scan rate = 25 mV s⁻¹.

3.3. Optimization of Analytical Parameters

Four accumulation media, namely phosphate buffer, acetate buffer, Britton-Robinson buffer and bicarbonate buffer were tested as accumulation media. The results showed that bicarbonate buffer was significant in terms of peak shape and sensitivity.

The effect of accumulation media pH on Cd²⁺-5-Br-PADAP complex formation was studied as shown in Fig. 5. The obtained results showed that, the best choice which had ability to give the best shape and highest current was pH=9.5. When the pH is lowered, 5-Br-PADAP will be protonated at the nitrogen and oxygen atoms which cause a reduction in the complexing ability of the 5-Br-PADAP. Therefore, we can expect that the most favorable conditions for complexation were those at higher pH. Therefore bicarbonate buffer (pH=9.5) was selected in the further experiments as accumulation media.

Fig. 5. DP voltammograms of 5-Br-PADAP-GO/CPE in cadmium solutions at different pH. Cadmium(II) concentration: 50 μgL⁻¹ Cd²⁺. Other conditions were the same as Fig. 4.

0.1 mol L^{-1} of HNO₃, H₂SO₄ and HCl solutions were tested as stripping medium. The best choice that has ability to give the best shape and highest current was HCl. The effect of HCl concentration on the shape of voltammograms was investigated, a small current was observed at 0.001 mol L^{-1} HCl solution which increased gradually up to 0.1 mol L^{-1} HCl solution and then decreased at higher concentrations. So, this concentration was used in all of the measurements.

The dependence of anodic peak current with the accumulation time for $15 \ \mu g L^{-1} \ Cd^{2+}$ was also investigated. The anodic peak current increased as the accumulation time increased between 0 and 7 min and after that, it became nearly constant due to the surface saturation. Hence, for all subsequent measurements accumulation time of 7 min was employed.

The influence of reduction potential on the anodic peak current of cadmium was investigated by varying the reduction potential from -0.1 to -1.9 V. Maximum peak currents were obtained when the reduction potential was set on -1.1 V. Hence, -1.1 V was employed as an optimum reduction potential for further studies. Also, the effect of reduction time was examined. The peak current of cadmium increased linearly with increasing reduction time up to 10 s and then became nearly constant. Therefore, a 10 s time was used for all measurements.

3.4. Calibration Curve, Detection Limit and Reproducibility

Standard solutions containing different concentrations of Cd²⁺ were prepared in bicarbonate buffer solutions (pH=9.5) and subjected to the optimized stripping voltammetric procedure. Voltammograms at these different concentrations are shown in Fig. 6. A linear calibration graph was obtained in the concentration range 0.25-210 μ g L⁻¹ and the detection limit was found to be 9.7 × 10⁻² μ g L⁻¹ Cd (II) and for five successive determinations of 10 and 150 μ g L⁻¹ Cd²⁺ relative standard deviations were 1.2 and 1.6 %, respectively.

Fig. 6. Differential pulse voltammograms of Cadmium(II) at 5-Br-PADAP-GO/CPE, Cadmium(II) concentration (a–w): 0.25, 15, 30, 50, 100, 150, 210 μg L⁻¹. Other conditions were the same as Fig. 4.

3.5. Interference Study

To check the selectivity of the proposed stripping voltammetric method for the Cd^{2+} ions, various metal ions as potential interferences, were tested. When the developed procedure was exploded for the determination of 10 µg L⁻¹ Cd(II) with optimum conditions, additions of 1.0 µg L⁻¹ each of Na(I), K(I), Zn(II), Ni(II), Hg (II), Mn(II), Fe(III), Bi(III), Ag(I), and Ca(II) had not an effect more than ±5 % on the cadmium currents. However, the presence of 1.0 µg L⁻¹ Pb(II) and Cu(II) was caused 12 and 9 % depressions of the Cd(II) peak current, respectively. These depressions can be due to compete these ions with Cd(II) to complex with 5-Br-PADAP at the electrode surface.

3.6. Real Sample Analysis

The developed method was applied to the determination of Cd^{2+} in drinking, tap and waste water samples. For water samples, this water was exchanged

with distillated water used for preparation of bicarbonate buffer (pH=9.5) and the resultant solution was analyzed as Section 2.6.

The concentration of Cd^{2+} content in samples was determined by calibration method using the modified CPE. The standard addition of cadmium was carried out to test the validity of the data. These results are shown in Table 1. The results showed that the 5-Br-PADAP-GO/CPE could be used for the determination of cadmium in real samples, with satisfactory recovery results of 98.0–101.7 %.

4. Conclusions

This paper showed that the 5-Br-PADAP is a useful ligand for the highly sensitive and selective determination of Cd^{2+} . Using GO in the composition of the carbon paste improves the conductivity of the modified electrode. By using both GO and 5-Br-PADAP, the selectivity and sensitivity of the modified electrode increased remarkably.

The DP voltammetry was used for determination of cadmium at 5-Br-PADAP-GO/CPE. In the present procedure by medium exchange the selectivity of the proposed voltammetric method increased. The calibration graph of Cd2+ linear from was 0.25-210 μg L⁻¹ with а slope factor of 0.1545 μ A(μ g L⁻¹)⁻¹ and correlation factor of 0.9996. The detection limit was $9.7 \times 10^{-2} \mu g L^{-1}$ which was lower than the concentration of Cd²⁺ in the real samples. The procedure presented in this study could be used for the determination of cadmium in water samples with good accuracy and precision.

Table 1. Determination of Cd(II) in various waters (n=4).

Sample	Present method (µg L ⁻¹) ^a	Spiked Cd ²⁺ (μg L ⁻¹)	Founded Cd ²⁺ (µg L ⁻¹) ^a	Recovery (%)
Tap water	N.D ^c	100.0	100.2±1.03	100.2
Drinking water	N.D ^c	100.0	101.1±1.20	101.1
Waste water ^b	24.9±0.9 5	100.0	125.8±2.1	100.7

^a Mean of three determinations ± standard deviation.

^b After dilution by 500 times.

^c Not detected.

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Finite Element Analysis for Single Cell Temperature Measurement Using PZT-Integrated Micro-capacitive Sensor

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Abstract: Analysis at a cellular level is an integral aspect that gives a clear understanding of a single cell's health condition as well as its internal metabolism. However, the field of genetics revealed nothing on single cell temperature analysis. In this paper, we proposed a noble technique for single cell temperature measurement using lead zirconate titanate (PZT) integrated microcapacitive sensor. The microcapacitive sensor has been modelled numerically and validated based on the current literatures. The sensor has been optimised by using parabolic geometry and integrated with PZT material for optimal separation between the sensor plates without having contact with the cell under investigation. The sensitivity of the PZT material integrated with the sensor was obtained as 0.0729 VmN⁻¹. Similarly, Saccharomyces cerevisiae cell has been modelled numerically and validated based on compression test experiment and Kedem-Katchalsky constitutive equation for fluid flow in a cell. 11.0381±0.0057 Nm⁻¹ and 108.9301±0.0084 MPa for stiffness and young's modules were obtained respectively. The PZT-integrated microcapacitive sensor and the Saccharomyces cerevisiae cell have been assembled for noninvasive temperature measurement. 0.5416±3.5581×10⁻³ nF and 0.7582±5.1366×10-3 µFcm⁻² were obtained for capacitance and dielectric constant value respectively for the Saccharomyces cerevisiae cell at normal atmospheric pressure which corresponds to 37 °C when a voltage of 1.0000 µvolt has been applied to the sensor. Saccharomyces cerevisiae cell dielectric constant of 1.5700×10⁻³±7.5000×10⁻⁴ µFcm⁻² has been obtained for each 5 ^oC change in temperature. Using the value above and interpolation technique the temperature of any single Saccharomyces cerevisiae cell can be obtained accurately. Temperature plays a vital role for characterising the health condition of the cell. In the future, the technique be a more effective and accurate supplement for the current biochemical method used disease diagnosis at cellular level.

Keywords: Disease diagnosis, Finite element analysis, Microcapacitive, Saccharomyces cerevisiae, Single cell analysis, Sensor.

1. Introduction

In present day research, the conventional microbiological techniques for cell analysis give information based on the average of the signals obtained from all the cells present in the sample under study [1]. However, in many fields of studies such as tissue engineering and cancer biology information obtained from signals averaging could result in erroneous conclusion [1-2]. This is because, the cells to be investigated may be the minority in the sample. As a result, behaviour of the majority will dominate the result. For this reason single cell analysis supplement the conventional microbiological techniques by providing results with high degree of precision and accuracy [2]. In point of fact single cell analysis has thrown more light for clear understanding of infections, drug response, diagnoses, biophysical and biochemical behaviour of the cell in general [1, 3-4]. Furthermore, using single cell analysis various parameters of the cell can be investigated [4-5]. However, among the various parameters of the cell, overall temperature of the cell play a vital role for the survival of the cell during cell division, gene expression etc [3, 5-8]. Moreover, the magnitude of the overall temperature of the cell can be used to characterise the health condition of the cell [9-12]. Abnormal cell such as cancerous cell possessed high rate of heat production than normal cell. In fact, some literatures reported that infected cell's temperature can rise up to 40 °C [3, 9-10]. But this significant information can only be obtained accurately with the aid of a sensor. For this reason temperature measuring devices dominate 75 to 80 % of the world sensor market [5].

Scientists have contributed immensely to Single cell analysis. As a result it has been an interesting area of research. Many attempts have been made in various literatures on how to measure the temperature of a single cell, because of its utmost importance in characterising a cell [3]. In [13] the authors proposed resonant thermal sensor for single cell temperature measurement via microfluidic charnel. The main drawback of the techniques is that, the accuracy of the measurement was affected due to the heat loss by the cell to the liquid in the microfluidic channel. [14], proposed an ultra-bright luminescent nanothermometer based on polymer encapsulated quantum dots. The nanothermometer was insensitive to both pH and ionic strength. On the other hand the nanothermometer proposed by [15] was insensitive only in the range of pH (4-10) and ionic concentration (0-500 mM). But the major drawback in both techniques was, the cell was exposed to radiation during temperature measurement which has significant effect on the cell metabolism in the next stage of analysis [5, 16-17]. Intracellular temperature mapping using fluorescent polymeric thermometer was proposed by [6, 17]. The fluorescent molecule was prepared and used as the temperature detector. According to [6] the molecular temperature detector was made to diffuse into the cell under investigation which may result to change in the molecular properties of the cell. For this reason, further analysis of the cell under investigation cannot produce accurate result. Fluidity manipulation of cell membrane for temperature detection technique was proposed by [7]. [8], proposed magnetofluorescent nanoscale temperature sensing particles. The technique was based on the cell endocytosis. The technique does not give information of the cell's temperature before the endocytosis. Furthermore, energy is utilized during endocytosis processes. For this reason, after the process the cell metabolism changes which affect the target parameter

(temperature) under investigation. In [4, 18], nanometre scale thermometry have been proposed to measure temperature in a living cell. The technique used laser to detect the colour of nitrogen vacancy which mapped to a particular temperature value based on idea of quantum spin mechanism. Biosensor for detecting thermal parameters based on internal living cell transport activities using nanomembrane have been proposed by [19]. The technique depend on the shifting effect caused by heat in the spectral bandgap of photoluminescence emitted from gallium nitride nanomembrane. As a result the induced laser heat causes significant effect on the heat contents of the cell under investigation. Indeed accurate temperature measurement may not be achieved. Measurement of temperature in a microscopic area around a living cell based on thermal activation technique have been proposed by [20]. Temperature detection based on cell imaging, staining and patterning using gold nanoclusters encapsulated in egg-white have been proposed by [21].

All the techniques reviewed above for single cell temperature measurement are invasive techniques. As a result, the cell under investigation suffers significant damage. Most of the techniques involve injecting foreign body to the cell sample cytoplasm, which causes significant changes in the cell's metabolism.

Furthermore, they cannot provide real-time data measurement due to image processing algorithm involved during temperature measurement. For this reason, the techniques cannot provide quick and accurate temperature measurement of a single cell without causing significant damage to the cell in general.

In this paper, we proposed a noble technique for single cell temperature measurement. The main advantage of our technique is that, it is a quick, accurate and non-invasive method contrary to the current method used for single cell temperature measurement. The technique could be very useful in the field of biotechnology, biomedical engineering, agriculture, medicine and pharmacy. The paper is organized in five (5) sections. In section one (1), introduction and existing research on single cell temperature measurement were presented. In section two (2), sensor idea and concept was presented. Finite element (FE) modelling, validation and optimisation of aluminium microcapacitive sensor and saccharomyces cerevisiae (yeast cell) were presented in section (3). Section (4) presents finite element temperature measurement of a single Saccharomyces cerevisiae using PZT-integrated microcapacitive Concluding remarks were sensor. presented in section (5).

2. Sensor Idea and Concept

The main function of the sensor is to measure the temperature of the single cell without causing any damage to the cell under investigation. Based on the cell's temperature information, the cell health condition can be characterised for fast, accurate and effective medical diagnosis. As most of the abnormal (e.g. cancerous) cells possessed high rate of heat production. The sensor designed concept can be summarised in Fig. 1. Furthermore, the sensor principal of operation was based on the variation of the capacitance of a capacitor caused by the change in the temperature of the dielectric material of the capacitor. The cell under investigation is used as the dielectric of the capacitor. As shown in Fig. 1, when the capacitor is fully charged the voltmeter reading will be equal to the source reading. As a result, the ammeter reading will be equal to zero, because electrons stop flowing in the circuit. The maximum current flow through the system and time taken for the ammeter reading to be zero are recorded respectively. The parameters obtained above give the quantity of the electrical charge and voltage from which the capacitance of the can be obtained in accordance with (1) [21]. Given as,

$$\frac{dQ}{dt} = C \frac{dV}{dt},$$
(1)

where Q, C and V are the charge stored, the capacitance and the applied dc-voltage respectively.

From the value of the capacitance (C), the dielectric constant (ϵ) of the cell can be computed. Since ϵ depends on temperature, the corresponding temperature of the cell under investigation can be obtained. Additionally, PZT material was integrated between the two plates to obtain the optimal separation distance between the two plates.

Fig. 1. PZT-integrated microcapacitive sensor design concept.

3. Finite Element Modelling, Validation and Optimisation of Microcapacitive Sensor and Saccharomyces Cerevisiae

ABAQUS software package (ABAQUS 6.14 CAE/CEL, Dassault Systemés, Pawtuckett, Rhode

Island, USA) is one of the famous, flexible and commercially available finite element analysis software. Because of the flexibility and availability of the above software it is commonly used in modelling, simulation, finite element analysis and data validation of biomedical, biotechnology and complex biomedical engineering analysis. The software was chosen for numerical cell temperature measurement and validation of data obtained based on the current literatures. Furthermore, the software gives the solution of complex equations generated during the analysis. We have reported that various attempts have been made to measure the temperature of a single cell, their disadvantages outweigh their advantages which has been highlighted in section I of this paper. For this reason, we proposed a noble technique to measure the temperature of a single cell. The modelling consists of three parts.

3.1. Microcapacitive Sensor Finite Element Modelling

The conductive plate of the microcapacitive sensor was designed numerically. Rectangular geometry was chosen for the conductive plate of the sensor with 7 μ m length, breadth of 4.5 μ m, based on the approximate size of the saccharomyces cerevisiae cell sample in accordance with the previously published work [1]. The thickness of the plate has been chosen as 100 nm in accordance with (2) proposed by [22]:

$$C_{xiang} = -\frac{\varepsilon_0}{\pi} [\ln\lambda + \ln(1 + 2 \cdot \lambda^4 + 15 \cdot \lambda^8 + 150 \cdot \lambda^{34} + \dots)), \quad (2)$$

where $\lambda = x_{iang}$ equation coefficient and can be obtained using (3) given as,

$$\lambda = \frac{1 - \sqrt{K'}}{2(1 - \sqrt{K'})},\tag{3}$$

where $K' = \tanh\left(\frac{\pi \cdot l}{2 \cdot h}\right), l$ is the length and h defines

the thickness.

However, all the dimensions adopted were scaled to micro and nano level [22]. The model has been built numerically using two dimension (2D) with desired dimensions and later transformed to 3D. Aluminium was chosen as the conductive plate of the sensor due to its electrical conductivity, lightness and resistance to corrosion [23]. The Young's modulus (70.00 GPa), Poisson's ratio (0.35) and molecular density (2.70×10^{-15} kgµm⁻³) of aluminium were adopted from [23]. The rectangular capacitive model obtained was confirmed by comparing with analytical data obtained and the result obtained by [22] as shown in Fig. 2.

Fig. 2. Rectangular capacitor modelling and validation.

3.2. Microcapacitive Sensor Finite Element Optimisation

The sensor was optimised by using parabolic geometry integrated with PZT material for accurate sensor positioning. Furthermore, the radius used was 2.5 μ m which is slightly larger than the based radius of the saccharomyces cerevisiae [1]. The PZT part of the sensor was modelled numerically based on the PZT general constitutive equation given by (4),

$$\begin{pmatrix} D_{1} \\ D_{2} \\ D_{3} \end{pmatrix} = \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix} \begin{pmatrix} T_{1} \\ T_{2} \\ T_{3} \\ T_{4} \\ T_{5} \\ T_{6} \end{pmatrix} + \begin{pmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ \varepsilon_{21} & \varepsilon_{22} & \varepsilon_{23} \\ \varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33} \end{pmatrix} \begin{pmatrix} E_{1} \\ E_{2} \\ E_{3} \\ E_{3} \end{pmatrix}$$
(4)

Since the PZT material was used as sensor not actuator (4) becomes,

$$\begin{pmatrix} D_1 \\ D_2 \\ D_3 \end{pmatrix} = \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix} \begin{pmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \\ T_5 \\ T_6 \end{pmatrix},$$
(5)

where D, d, ε and E are the electrical polarisation vector, the piezoelectric coefficient matrix, the stress vector, the electrical permittivity matrix and the electrical field vector respectively.

The material properties of PZT-5H were adopted from [1] as shown in Table 1. The PZT model has been validated by applying force along the poling axis of the PZT and the corresponding voltage was obtained as shown in Fig. 3. The sensitivity of the PZT is $0.0693 \text{ mV}\mu\text{m}\mu\text{N}^{-1}$ which shows that our model is in good agreement with the result obtained by [1].

Table 1. PZT-5H MATERIAL Properties.

Para- meter	Matrix of parameters for polarisation along y-axis	Units
Comp liance	$\begin{bmatrix} 12.6 & 8.41 & 7.95 & 0 & 0 & 0 \\ 8.41 & 11.7 & 8.41 & 0 & 0 & 0 \\ 7.95 & 8.41 & 12.6 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2.3 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2.325 & 0 \\ 0 & 0 & 0 & 0 & 0 & 2.3 \end{bmatrix} \times 10^{-4}$	μN/μm²
Stress coef- ficient	$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 17 \\ -6.5 & 23.3 & -6.5 & 0 & 0 & 0 \\ 0 & 0 & 0 & 17 & 0 & 0 \end{bmatrix} \times 10^{-12}$	C/µm ²
Dielec tric cons- tants	$\begin{bmatrix} 1.505 & 0 & 0 \\ 0 & 1.302 & 0 \\ 0 & 0 & 1.505 \end{bmatrix} \times 10^{-14}$	C/Vµm

Fig. 3. (a) PZT material model and (b) Voltage-Force relationship plot for model validation.

Fig. 4 shows the comparison of the capacitance (C_{Analytical} C_{Rectangular} Geometry and C_{Parabolic}) plot against length of the plate per separation between the plates (l/d). However, for parabolic geometry the major radius (R1) and minor radius (R2) were used in place of l and d respectively. Additionally, air was used as dielectric material at room temperature. Conversely, the contribution of the PZT dielectric for parabolic model was not taken into account based on considerable assumption. As a result, the model was compared with both analytical and previously published work for validation. The model is in agreement with the result obtained by [22-23].

Fig. 4. Comparison of the capacitance plot against length of the plate per separation between the plates (l/d).

3.3. Finite Element Modelling and Validation of Saccharomyces Cerevisiae (Yeast Cell)

The FE Cell sample was modelled using Saccharomyces cerevisiae material properties. Saccharomyces cerevisiae was chosen because it has identical life cycle with the mammalian cell. For this reason, it is used to investigate regenerative diseases (fibroid, cancer etc). Contrary to red blood cell of humans, Saccharomyces cerevisiae has clearly defined cell wall. But general constitutive equation governing the behaviour of human red blood cell is applicable to Saccharomyces cerevisiae based on significant assumption [1]. In this paper the FE model of Saccharomyces cerevisiae with cytoplasm (interior layer) and cell wall (exterior layer) was designed numerically. The following parameters were used and obtained from [1]: Thickness of 90 nm, radius in the range of 5.0 to 4.5 µm, Young's modulus of, cytoplasm density of 1 gmL⁻¹, cell wall density of 1.084×10⁻¹⁵ kgµm⁻³, Young's modulus of 112 MPa and 0.5 as Poisson's ratio respectively. The model was validated based on compression test experimental data and Kedem-Katchalsky constitute equation for fluid flow in a cell given by (6) [1],

$$\frac{dV}{dt} = k_t A \left(\Delta P - \Delta p \right), \tag{6}$$

where V defines instantaneous volume, k_t is the permeability constant, t is time, ΔP is the change in hydrostatic, Δp is the osmotic pressure and A is the available area.

Fig. 5 shows the results obtained from the compression test experiment which shows that our *Saccharomyces cerevisiae* FE model agrees with the model obtained by [1].

Fig. 5. Modelling and validation *Saccharomyces cerevisiae* cell based on compression test experiment.

4. Finite Element Temperature Measurement of a Single Saccharomyces Cerevisiae Using PZTintegrated Micro-capacitive Sensor

We have modelled, validated and optimised the PZT-integrated micro-capacitive sensor and *Saccharomyces cerevisiae* cell in the previous section. In this section, the single *Saccharomyces cerevisiae* cell temperature measurement has been conducted using finite element method. The assembly of the

PZT-integrated micro-capacitive sensor and *Saccharomyces cerevisiae* cell was carried out numerically for single cell temperature measurement as shown in Fig. 6.

Fig. 6. Assembly of the PZT-integrated micro-capacitive and Saccharomyces cerevisiae cell in ABAQUS for single cell temperature measurement sensor.

Variation of temperature affect the dielectric material of a capacitor [22]. As a result, the change in dielectric material of the PZT-integrated microcapacitive sensor has been linked with the variation of temperature of the Saccharomyces cerevisiae cell under investigation. The variation in temperature of the Saccharomyces cerevisiae cell occur because of the change in the internal metabolism of the cell under investigation. Virus and bacteria attack as well as malignancy changes the internal metabolism of a cell, which causes variation in the temperature of the cell [24]. For this reason, the temperature of the Saccharomyces cerevisiae cell can be measured from the corresponding value of the capacitance obtained when a considerable amount of voltage has been applied to the sensor.

The value of the quantity of charge stored in the PZT-integrated micro-capacitive sensor and the corresponding capacitance value obtained in ABAQUS when 1.0000 µvolt has been applied to the sensor shown in Fig. 7. Even though, *Saccharomyces cerevisiae* cell has been subject to 1.0000 µvolt, the electrical activities of the cell counter balance the field effect [24]. Furthermore, the temperature value has been changed in step of 5 $^{\circ}$ C to have significant change

in the value of the capacitance of the sensor under normal atmospheric condition. Using the sensor geometry based on reasonable assumption the dielectric constant of the *Saccharomyces cerevisiae* cell has been obtained as shown in Fig. 8.

Fig. 7. Saccharomyces cerevisiae cell temperature measurement at normal atmospheric condition.

Fig. 8. *Saccharomyces cerevisiae* cell temperature measurement based on the variation of the capacitance and dielectric of the cell at normal atmospheric condition.

Furthermore, between 30 °C to 37 °C there is significant increase in the dielectric constant values of the cell because that is the optimal temperature for the *Saccharomyces cerevisiae* cell growth. In fact, the dielectric constant value is function of area. From Fig. 8, at 37 °C using interpolation technique and measure of dispersion the capacitance and the dielectric constant value of the *Saccharomyces cerevisiae* cell are $(0.5416\pm3.5581\times10^{-3})$ nF and $(0.7582\pm5.1366\times10^{-3})$ µFcm⁻² respectively. The value of the dielectric constant obtained is in good agreement with the value obtained by [24]. Furthermore, we observed that at 0 °C the rate metabolism of *Saccharomyces cerevisiae* cell is very low. For this reason, a very low value of the dielectric

constant has been obtained. Similarly, at high temperature around 50 °C, when the cell is dead an appreciable value of dielectric constant has been obtained because the sensor used the dead cell as dielectric material. For 5 °C change in temperature the corresponding change in value of the dielectric constant of *Saccharomyces cerevisiae* cell is $(1.5700 \times 10^{-3} \pm 7.5000 \times 10^{-4}) \,\mu\text{Fcm}^{-2}$. Indeed, using the value above and interpolation technique the temperature of a single *Saccharomyces cerevisiae* cell can be obtained accurately.

5. Conclusions

This research work demonstrates for the first time how to measure the temperature of a single cell using PZT-integrated micro-capacitive sensor. The sensor was successfully modelled using rectangular geometry validating models from [2-3, 22]. The model was optimised using parabolic geometry integrated with PZT material for optimal separation between the plates. Similarly, Saccharomyces cerevisiae cell was modelled and confirmed using previous work [1]. The models were assembled for single Saccharomyces cerevisiae cell non-invasive temperature measurement. Further investigation established the effect of temperature on the capacitance of the capacitive sensor, which is directly proportional to the dielectric constant provided other physical quantities remain unchanged. The main advantage of our technique is that, it is a non-invasive method contrary to the current method used for single cell temperature measurement. For this reason, further investigation can be carried out using the same cell sample. The researcher's technique proves to be quick and accurate compared to the current conventional methods. In the future, the technique will supplement current biochemical method for disease diagnosis at cellular level for effective treatment.

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Molecular Doping on Epitaxial Graphene by Gaseous Surface Adsorbents: Influence of Interband Scattering

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Abstract: We investigate molecular adsorption doping by electron withdrawing NO₂ and electron donating NH₃ on epitaxial graphene grown on C-face 6H-SiC substrates. We reconcile models describing the conductivity of graphene at low and high frequencies in the relaxation time approximation. These equations are applied to develop theoretical model for adsorption of NO₂ and NH₃ molecules on an epitaxial graphene surface probed by infrared reflectance, a non-destructive technique for transport studies in graphene. We separate the intraband and interband scattering contributions to the electronic transport under gas adsorption. We find that only by including a significant interband (intraband) contribution can measured reflectance be fit accurately at low (high) frequency regime. Interband relaxation times as short as \sim 0.1 fs are obtained under gas adsorption, much shorter than previously assumed (\sim 100 fs), leading to a breaking of the usual universal conductivity observed in purer samples. This method can also calculate percentage charge transfer by NO₂ to graphene (1 \sim 2 %) and NH₃ to graphene (0.01 \sim 0.1 %). Finally, this transport behavior indicate that, under gas adsorption, the influence of interband scattering cannot be neglected, even at DC

Keywords: Graphene, Molecular adsorption doping, Interband Scattering, Gas adsorption

1. Introduction

Graphene is a revolutionary zero bandgap nanomaterial that demonstrates remarkable properties, such as high electron mobility [1], the highest Young's modulus ~1 TPa [2], the highest thermal conductivity of any known material [3] and single molecule sensitivity to gases [4]. This unique electronic properties arises from it's massless Dirac-like linear dispersion ($E = hkv_F$) of electrons [1], where E is the energy, *h* is the plank's constant, *k* is the Fermi wave vector and v_F is the Fermi velocity (Fig. 1(a). This linear dispersion relation is in contrast to the traditional quadratic dispersion commonly exhibited by most semiconductors; introduce a new class of electronic material for sensing and device application. This truly 2D structure can be doped to high value of electron and hole concentration either by applying external voltage, much like an FET or with the molecular and adsorption doping. Molecular doping on both exfoliated and epitaxial graphene has been successfully studied. The charge impurity of exfoliated graphene was studied by J. H. Chen, *et al.*, [5] where graphene was doped by potassium and Tetra-cyanoquino-di-methane (TCNQ) at ultra high vacuum. Potassium doping on epitaxial graphene has also been studied by A. Bostwick, *et al.* [6], where growth, EG/SiC interface and electronic property has been discussed. These kinds of control over electrical properties of material are the heart of modern electronics such as FET and sensors.

The good sensor properties of carbon nanotubes are already known for some time, [7] but recently, the

possibility to use graphene as a highly sensitive gas sensor was also reported [4]. Graphene on SiC substrate (EG) offers the added advantage of integrating sensors and readout circuits on the same chip, that are also suitable for harsh environment operation, taking advantage of the wide band gap of SiC [8]. It was shown that the increase in graphene charge carrier concentration induced by adsorbed gas molecules can be used to make highly sensitive sensors, even with the possibility of detecting individual molecules. These excellent sensor properties of graphene are due to two important facts:

1) Graphene is a two-dimensional crystal with only a surface and no volume, which maximizes the effect of surface dopants;

2) Graphene is highly conductive and shows metallic conductance even in the limit of zero carrier density.

These sensor properties are based on changes in the resistivity due to molecules adsorbed on the graphene sheet that act as donors or acceptors. It is well established that EG surface conductivity can be varied by molecular adsorption doping where conductivity is a tradeoff between carrier concentration and scattering [9].

The sensitivity of exfoliated graphene to NH_3 and $NO_2[10]$ and that of epitaxial graphene (EG) [11] have been established by molecular adsorption doping where the adsorbent NH_3 and NO_2 acts as electron donating and withdrawing characteristics respectively. Thus EG surface electron concentration can either increase or decrease depending on whether the adsorbent is electron donating or withdrawing. These adsorbents can also influence carrier scattering, all of which change the surface conductivity. In our earlier paper [12] we established a change of conductivity due to molecular adsorption doping by amperometric (DC) measurements. In this paper we emphasize carrier transport studies through Fourier transform infrared (FTIR) measurement for molecular adsorption doping within the frequency range of 10 THz to 100 THz. Theoretically, we account for the influence of surface impurities on the conductivity of EG by molecular gas adsorption [10] using the Boltzmann picture, experiment. consistent with our Thus the reconciliation of EG conductivity of low and high frequency is important to investigate the transport properties in mid IR regime.

2. Theory

2.1. Derivation of EG Conductivity

A detailed model of the electrical and optical conductivity from direct current (DC) to the infrared is required to enable this investigation. In any material, the conductivity can be divided into two components, intraband and interband conductivities. Intraband conductivity refers to the traditional Drude-Sommerfeld type conductivity involving free electrons (holes) in the conduction (valence) band. Scattering events here only move carriers within the same band named intraband scattering. Interband conductivity accounts for processes where carriers can move between bands, such as direct optical absorption and carrier recombination. Scattering events here lead to carriers changing bands known as interband scattering. Fig. 1(a) illustrates these two conduction modes in EG where Fermi level position is also indicated.

Fig. 1. (a) Plot of EG linear dispersion relation ($E = hkv_F$), Fermi level E_f is shown and intra and interband transition regime is indicated; (b) Shows reflection from EG where graphene is considered between air and SiC interface; (c) Experimental set-up for IR reflection spectroscopy for molecular adsorption measurement.

Gusynin, *et al.*, [13] adopt a Kubo-Green formalism to describe the interband and intraband conductivity of graphene. While this is a complete and rigorous description, it is somewhat complex, and

hides the "Boltzmann-like" diffusive transport inherent in it. Furthermore, in the original formulation [14], the relaxation times used for the interband and intraband terms are identical. While this is a good starting point, the measurements presented later in the paper show that this is not accurate. In fact, there is no a priori reason why the relaxation times for the two very different conduction modes should be the same. Introducing separate scattering times τ_{intra} and τ_{inter} for intraband and interband conduction modes respectively, these equations for the optical conductivity can be written as [13];

$$\sigma_{\operatorname{int} ra} = \frac{e^2}{\pi \hbar} \frac{i}{\omega + i / \tau_{\operatorname{int} ra}} \int_{-\infty}^{+\infty} d\varepsilon \left(-\frac{\delta f(\varepsilon - \varepsilon_f)}{\delta \varepsilon}\right) \varepsilon^2 \frac{\theta(\varepsilon^2)}{|\varepsilon|},$$
(1)

$$\sigma_{\text{int}er} = i \frac{e^2(\omega + i/\tau_{\text{int}er})}{\pi} \int_0^{+\infty} \frac{d\varepsilon [f(\varepsilon - \varepsilon_f) - f(-\varepsilon - \varepsilon_f)]}{(2\varepsilon)^2 - \hbar^2 (\omega + i/\tau_{\text{int}er})^2},$$
(2)

where e is the electronic charge, ε is the energy variable over which integration takes place, $\varepsilon_{\rm f}$ is the Fermi level, ω is the frequency of the incident electromagnetic radiation, the Fermi-Dirac $f(\varepsilon) = [\exp(\varepsilon / kT) + 1]^{-1}$ is distribution function, k is the Boltzman constant $1.3806503 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2}\text{K}^{-1}$ and θ is the Heaviside step function. We note that throughout this paper, SI units are used, unless otherwise indicated.

2.2. Intraband Conductivity

The DC intraband conductivity can be understood in the Boltzmann transport picture from Equation (1). By assuming that the temperature is low i.e. $\varepsilon_f \gg kT$, the Fermi functions, f, in Equation (1) can be replaced by step functions, leading to the approximation,

$$\int_{-\infty}^{+\infty} d\varepsilon \left(-\frac{\delta f(\varepsilon - \varepsilon_f)}{\delta \varepsilon}\right) \varepsilon^2 \frac{\theta(\varepsilon^2)}{|\varepsilon|} = \varepsilon_f$$
(3)

Putting this value in eq-1 and considering $\omega = 0$ we get the DC conductivity as follows

$$\sigma_{intra} = \frac{e^2 \tau_{intra} \varepsilon_f}{\pi \hbar}$$
(4)

Carrier concentration is given by...

$$n = \int_{0}^{\infty} D(\varepsilon) f(\varepsilon - \varepsilon_{F}) dE$$
(5)

where D(ε) is the density of states in graphene. $D(\varepsilon) = 2\varepsilon / \pi (\hbar v_F)^2 \approx 1.46 \times 10^{14} \text{ E cm}^{-2}.$

Replacing this value in Equation (4) and using Fermi Dirac distribution $E = hkv_F$), we get...

$$\sigma_{\text{int}ra} = ne^2 v_f^2 \tau_{\text{int}ra} / \varepsilon_f = ne^2 \tau_{\text{int}ra} / m_{rel} = ne\mu,$$
(6)

where we have used the relativistic relation $\mathcal{E}_f = m_{rel}v_f^2$ in the last step for the relativistic masslike term m_{rel} . Thus, the Kubo formula can be thought of as a relaxation time modification to the Boltzmann conductivity and shows the equivalence of the 2 pictures.

2.3. Interband Conductivity

We begin by assuming that there is negligible broadening of the interband transitions i.e. long τ_{inter} . With this assumption, and by taking low temperatures, giving $\varepsilon_f >> kT$, we can replace the Fermi functions in Equation (2) above with step functions.

$$\sigma_{\text{inter}} = \frac{ie^2\omega}{4\pi} \int_0^{\infty} \frac{d\varepsilon [f(\varepsilon - \varepsilon_f) - f(-\varepsilon - \varepsilon_f)]}{(\varepsilon)^2 - (\hbar\omega/2)^2}$$
$$= \frac{ie^2\omega}{4\pi} \int_{\varepsilon_f}^{\infty} \frac{d\varepsilon}{(\varepsilon)^2 - (\hbar\omega/2)^2} , \qquad (7)$$
$$= \frac{ie^2\omega}{4\pi} \frac{1}{\hbar\omega} \ln(\frac{\varepsilon_f - \hbar\omega/2}{\varepsilon_f - \hbar\omega/2})$$

where we have used partial fractions to evaluate the final step. The frequency term ω , in the coefficient cancels out, leaving the logarithmic term. In the limit $\omega \rightarrow \infty$, $\sigma_{\text{inter}} \rightarrow e^2/4\hbar$, independent of frequency, the so-called universal conductivity of graphene [15].

Now, we reintroduce the interband broadening through the relaxation time approximation. This is done by replacing $\omega \longrightarrow \omega + i / \tau_{inter}$. Now, again in the limit $\omega \rightarrow \infty$, we recover the universal conductivity. However, when $\omega \ll \tau_{inter}^{-1}$, the conductivity can deviate significantly from the universal conductivity. In fact, for $\tau_{inter} = 5 fs$, a reasonable value in some situations (more data below), the conductivity can deviate significantly from the universal value even in the infrared and visible regimes.

We thus consider the low frequency regime i.e. $\omega \longrightarrow 0$. In this limit,

$$\sigma_{\text{inter}} = \frac{ie^2}{4\pi\hbar} \ln(\frac{\varepsilon_f - i\hbar/2\tau_{\text{inter}}}{\varepsilon_f + i\hbar/2\tau_{\text{inter}}}) = \frac{ie^2}{4\pi\hbar} \ln(e^{-2iX}) = \frac{e^2X}{2\pi\hbar},$$
(8)

where $X = \arctan(\hbar/2\varepsilon_f \tau_{inter})$. We now make the assumption that $X \ll 1$ i.e., ε_f is large >> kT i.e. low temperature and/or τ_{inter} is long. This is a reasonable assumption, for typical values of $\varepsilon_f \sim 0.2$ eV and τ_{inter} as short as 5fs. This allows us to approximate $X = \arctan(\hbar/2\varepsilon_f \tau_{inter}) \approx \hbar/2\varepsilon_f \tau_{inter}$. Thus, Equation (8) becomes

$$\sigma_{\rm inter} = \frac{e^2}{4\pi\varepsilon_f \tau_{\rm inter}},\tag{9}$$

which is identical to the result obtained by Liu, *et al.*, [16] using a kinetic approach for DC. Thus, the equivalence of the full optical model and the DC kinetic model for the interband conductivity is demonstrated. A key conclusion of Equation (9) is that even at DC i.e., $\omega = 0$, there is a non-negligible interband contribution to the conductivity of graphene. We will later present experimental evidence for this behavior.

2.4. Reflection

Considering graphene at the interface between two dielectrics (shown in Fig. 1(b) with dielectric functions \mathcal{E}_1 and \mathcal{E}_2 , the total reflectivity is given by [17]

$$R = \frac{\left| \left(\sqrt{\varepsilon_{1} \varepsilon_{2}(\omega) \varepsilon_{0}} / \alpha \right) + \frac{\sqrt{\varepsilon_{1}} N \sigma(\omega) \times \cos(\Phi 1)}{c} - \varepsilon_{1} \varepsilon_{0} \right|^{2}}{\left| \left(\sqrt{\varepsilon_{1} \varepsilon_{2}(\omega) \varepsilon_{0}} / \alpha \right) + \frac{\sqrt{\varepsilon_{1}} N \sigma(\omega) \times \cos(\Phi 1)}{c} + \varepsilon_{1} \varepsilon_{0} \right|^{2}}$$
(10)

where $\alpha = \frac{\sqrt{1 - [(\frac{n_1}{n_2} \sin \Phi 1)]^2}}{\cos \Phi 1}$ n₁ and n₂ are the refractive

index of air and SiC respectively, $\sigma(\omega)$ is the total conductivity, $\boldsymbol{\mathcal{E}}_0$ is the free space permittivity (~8.854×10⁻¹² F/m). For EG on SiC substrates, $\boldsymbol{\mathcal{E}}_1$ is the permittivity of air (~1) and $\boldsymbol{\mathcal{E}}_2$ is the permittivity of SiC, which is a function of wavelength, given by [18]

$$\varepsilon_2(\omega) = \varepsilon_{\infty} \frac{\omega^2 - \omega_{LO}^2 + i\Gamma_1\omega}{\omega^2 + \omega_{TO}^2 + i\Gamma_2\omega}$$
(11)

where $\mathcal{E}_{\infty} = 6.5$ is the positive ion core background dielectric constant, ω_{LO} is the longitudinal optical phonon frequency ($\omega_{LO} = 972 \text{ cm}^{-1}$), ω_{TO} is the transverse optical phonon frequency ($\omega_{TO} = 796 \text{ cm}^{-1}$). $\Gamma_{1,2}$ describes the broadening of the phonon resonances, typically 5-60 cm⁻¹, where the higher values are due to free-carrier absorption.

Within this theoretical framework, we investigate the carrier transport by FTIR reflection spectroscopy, while theory matches with experimental results to extract various transport parameters, including the influence of interband scattering, which is nonnegligible at IR frequencies and high surface impurity concentrations. Finally we show the role of interband scattering on impurity concentration.

3. Experimental

Epitaxial growth of large-area graphene by thermal decomposition of commercial <0001> 4H and 6H SiC substrates at high temperature and vacuum has been demonstrated [19]. This produces EG a few monolayer, ML to >50 ML thick, depending on growth conditions. In our experiments, EG was grown on commercial n⁺ 8⁰ off axis 4H-SiC substrates on C-face, nitrogen doped $\sim 10^{19}$ /cm³. 1 cm×1 cm samples were degreased using trichloroethylene, acetone and methanol respectively. They were then rinsed in DI water for three minutes. The samples were finally dipped in HF for two minutes to remove native oxide and rinsed with DI water before being blown dry. They were then set in the crucible in an inductively heated furnace where high vacuum was maintained (<10⁻⁶ Torr) and baked out at 1000 ⁰C for 13 to 15 hours. The temperature was slowly raised to the growth temperature (1250-1400°C). All growths were performed for 60 minutes before cooling to 1000 °C at a ramp rate of 7~8°C/min and eventually to room temperature. Slow temperature ramps were utilized to minimize thermal stress on the samples.

For this study, our focus is on epitaxial graphene on C-face because defects have been attributed to the EG grown on C-face SiC [20]. Fourier Transform Infrared reflection (FTIR) spectra gives the differential reflectance with respect to a reference. For EG reflection spectra, SiC substrate used as a reference for the respective gas medium. Defects on EG layer (grown on C-face SiC) allow diffusion of gas through the defects point justifies the similar reference maintain under particular gaseous medium.

After growth AFM (atomic force microscopy) was used to investigate the EG surface morphology with and the morphology is similar to that observed by others [1, 12, 19]. Raman measurements were carried out on EG on both carbon (C) and silicon (Si) faces. Micro-Raman spectroscopy using a 632 nm laser shows the G peak (~1590 cm⁻¹), D peak (~1350 cm⁻¹) and 2D peak (~2700 cm⁻¹) characteristic of EG [21]. The ratio of intensities of the D-peak to G-peak, I_D/I_G ≤ 0.2 demonstrates the high quality of our graphene [21]. X-ray photoelectron spectroscopy (XPS) measurements were done to obtain the thickness [22] in monolayer's (ML) on EG. The thickness extracted by XPS was consistent with our FTIR measurements [12].

Fourier transform infrared reflection (FTIR) measurements (2.5 μ m to 25 μ m wavelength) were carried out with a blank SiC substrate, cut from the same wafer as the grown samples, as the reference (shown in Fig. 1(c). So we find differential reflectance of EG with respect to SiC substrate. Our previous work indicate that this method can be applicable to find EG thickness in no of monolayers (ML's), scattering time (τ), and Fermi level (E_f). Thickness measurement using this method is consistent with XPS measurements as explained et.al. Daas [12]. In this work, FTIR measurement was carried out as the same process described above but the chamber was filled

with the required adsorbent gas (Fig. 1(c). Reference was taken with N_2 environment (known as inert gas) and corresponding IR reflection was taken in $N_2/NO_2/NH_3$ environment consequently. All reflectance measurement presented here are the differential reflectance with respect to the SiC substrate. A more detailed analysis of this data, along with our developed theory allows the extraction of the influence of interband scattering as well, which is nonnegligible at IR frequencies and high surface impurity concentrations.

4. Result and Discussion

NO₂ is a strong oxidizer with electron withdrawing capability, and is expected to decrease electron carrier concentration on the EG surface [23], while the converse is true for NH₃ as it is electron donating [24]. However, our measurements are based on EG grown on C-face SiC, which is thicker (>8ML), much greater than the 1ML screening length in graphene [25]. Thus, this layer is expected to be close to electrically neutral i.e. the Fermi level is close to the Dirac point (K and K' in the Brillouin zone). Therefore, carrier concentration will increase in both the cases regardless of whether the adsorbent is electron withdrawing or electron donating.

Polar molecules [11] change EG conductivity by a) inducing carriers in the EG and b) increasing scattering i.e. decreasing mobility. Scattering (τ) includes both intra and interband scattering, responsible for inter and intra band conductivity respectively [11]. Increase or decrease of conductivity is a tradeoff between carrier concentration (Equation (5) and scattering. Thus, it is critical to investigate the role of E_F and τ in response to gas adsorption.

Fig. 2 shows the IR reflection spectra for 9, 22 and 34 ML EG in N_2 , NH_3 and NO_2 environment where we find that reflectance (indicative of conductivity, with higher conductivity leading to higher reflectance) changes for different gases due to adsorption of surface impurities. Reflectivity decreases both in NO_2 and NH_3 environments compared to N_2 with NO_2 showing greater decrease than NH_3 . Because, NH_3 has lower adsorption energy which allows it to both charge

interacting and non-interacting configuration [26], whereas NO₂ has higher adsorption energy $(0.3\sim0.4 \text{ eV})$ [27], which forces it to accept electrons in any adsorption configuration [26]. We extract ML, E_F and intra and inter band scattering time by matching experimental data with the theory (Table 1). We also used previously developed mathematical model [12] to account for impurity adsorption where we match optical conductivity [16] at high and low frequency with conductivity in the Random Phase approximation (RPA) to extract surface impurity concentration, n_i by

$$\sigma_{T=0}^{RPA} = \frac{e^2}{\pi h} \left[\frac{n_s}{n_i G[4r_s / (2 - \pi r_s)]} + \frac{n_i F[4r_s / (2 - \pi r_s)]}{4n_s} \right], \quad (12)$$

where h is the Planck's constant, n_s is the surface carrier concentration, r_s , G and F function are defined as below.

Fig. 2. (color online): Shows the IR reflection measurement while experimental data fits with the mathematical model. Extracted parameters are indicated in Table 1.

No of Layer	Gas	Fermi level (meV)	Impurity (cm ⁻²)	Intra band scattering time (s)	Inter band scattering time (s)
	N_2	25 ± 2	$(2 \pm 0.5) \times 10^{11}$	$(2.8 \pm 0.9) \times 10^{-13}$	$(4.3 \pm 2.7) \times 10^{-14}$
34	NH ₃	30 ± 2	$(6 \pm 1) \times 10^{12}$	$(7.5 \pm 2) \times 10^{-15}$	$(2 \pm 1) \times 10^{-15}$
	NO ₂	35 ± 2	$(2 \pm 0.6) \times 10^{13}$	$(1.4 \pm 1) \times 10^{-15}$	$(3.5 \pm 2) \times 10^{-16}$
22	N_2	45 ± 2	$(3 \pm 0.5) \times 10^{11}$	$(1.5 \pm 0.3) \times 10^{-14}$	$(2.3 \pm 0.1) \times 10^{-14}$
	NH ₃	65 ± 2.5	$(7.5 \pm 1) \times 10^{12}$	$(6 \pm 3) \times 10^{-15}$	$(1 \pm 0.01) \times 10^{-15}$
	NO ₂	95 ± 3	$(6 \pm 1) \times 10^{13}$	$(9 \pm 0.3) \times 10^{-16}$	$(2 \pm 0.7) \times 10^{-16}$
9	N_2	70 ± 4	$(5.1 \pm 0.5) \times 10^{11}$	$(1.5 \pm 0.1) \times 10^{-13}$	$(2.2 \pm 0.4) \times 10^{-14}$
	NH ₃	90 ± 4	$(5.5 \pm 1) \times 10^{13}$	$(9 \pm 1) \times 10^{-16}$	$(3.6 \pm 1) \times 10^{-16}$
	NO ₂	120 ± 4	$(1.5 \pm 0.8) \times 10^{14}$	$(4\pm 1) \times 10^{-16}$	$(2\pm 1) \times 10^{-16}$

Table 1. Shows extracted parameter while experiment matches with theory.

$$r_{s} = \frac{e^{2}}{4\pi\varepsilon_{0}\varepsilon_{SiC}v_{F}\hbar},$$
(13)

where e is the electron charge 1.6×10^{-19} C, v_F is the Fermi velocity 1.1×10^6 m/s, \mathcal{E}_{SiC} is the dielectric constant of SiC, which has different values for high frequency ($\mathcal{E}_{SiC} \sim 6.5$) and low frequency ($\mathcal{E}_{SiC} \sim 9.52$) regime and G and F function defined [16] as,

$$G(x) = \frac{x^2}{8} \int_{0}^{2\pi} \frac{\sin^2 \theta}{(\sin \frac{\theta}{2} + x)^2} d\theta$$

and (14)
$$F(x) = \frac{x^2}{8} \int_{0}^{2\pi} \frac{(1 - \cos \theta)^2}{(\sin \frac{\theta}{2} + x)^2} d\theta$$

Considering two limiting values of SiC dielectric constant (high frequency~6.5 and low frequency~9.52), two different values of r_s (high frequency~0.31 and low frequency~0.21) were calculated [18]. For the high frequency $r_s = 0.31$ was used for the conductivity

$$\sigma_{T=0}^{RPA}[high frequency] = \frac{e^2}{\pi h} \left[\frac{n_s}{n_i G[4r_s / (2 - \pi r_s)]} \right] (15)$$

matching with the optical conductivity to extract impurity concentration, n_i . A similar procedure was used for the low frequency side where $r_s \sim 0.21$ arises

from $\mathcal{E}_{SiC} \sim 9.52$ while considering

$$\sigma_{T=0}^{RPA}[lowfrequency] = \frac{e^2}{\pi h} \left[\frac{n_i F[4r_s / (2 - \pi r_s)]}{4n_s} \right]$$
(16)

 n_i extracted at both these frequency regimes was consistent. For further confirmation, we calculate intra and inter band scattering from n_i using equations presented elsewhere [16] and was found to be consistent with our extracted data within the experimental error limit.

Table 1 show the extracted carrier transport parameters for 34, 22 and 9ML samples in gaseous medium while experiment matches with theory. E_f and τ was extracted as a fitting parameter while n_i was extracted by conductivity matching both high and low frequency regime (discussed above). With N₂ gas, 34ML samples shows Fermi level of ~25 meV, close to neutral because our EG is thick. Similarly 22 and 9ML samples shows increase in Fermi level to 45 meV and 70 meV respectively because of thinner layer compared to 34ML, comparable to EG screening length ~1ML. As N₂ is an inert gas and should not contribute any impurity on the EG surface. Our extracted parameters indicate a surface impurity concentration due to N_2 gas is of $2 \sim 5 \times 10^{11} \text{cm}^{-2}$, fairly consistent with an ex-situ sample that has not had any degassing or other processing performed on it.

For NH₃ and NO₂, the surface impurity concentration is higher than N₂ because of the nature of the gas interaction (electron donating and withdrawing ability) with the carriers on the EG surface (Fig. 3). Increase in Fermi level position compared to N₂ in both the cases indicates more surface impurity concentration due to gas adsorption. For 34ML sample, change is Fermi level is very small (~5 meV in NH₃ and 10 meV in NO₂) indicates that thicker EG layer behaves more like neutral layer because of EG screening length is only ~1 ML. For 22 and 9 ML sample Ef changes are noticeably greater indicates the sensitivity of EG as presented by other researchers [16]. This thickness dependent trend clearly supports the single molecule sensitivity of single layer graphene described elsewhere [4]. E_f changes are greater in NO2 compared to NH3 attributes more charge transfer by NO2 compared to NH3. Changes of E_f is also supported by other potentiometric measurements Qazi, et al., [28] where surface work function (SWF) changes are directly measured and Fermi level change was extracted from there.

Fig. 3. (color online) (a) Impurity concentration on EG layer due to molecular adsorption. It shows that NO₂ has the charge transfer ratio of 1-2 % whereas NH₃ has only 0.01-0.1 %; (b) shows the animation of molecular adsorption through EG defect position.

We also extract scattering time (τ) through our model as theory fits with the experiments. Table 1 indicates that, both τ_{intra} and τ_{inter} shortens, due to more scattering from the adsorbed impurity. As overall conductivity is the tradeoff between carrier concentration (indication of E_f changes) and scattering (both intra, τ_{intra} and interband, τ_{inter}), So despite of the method developed by Nomani, *et al.*, [29], our method signifies the complete picture of conductivity changes with a good agreement as presented by other publications [30].

Overall conductivity decreases both for NH_3 and NO_2 compared to N_2 environment. With NO_2 , overall conductivity decreases more than NH_3 despite a strong

increase in carrier concentration (Fig. 3), indicating that the EG surface has greater affinity for NO₂ adsorption, leading to much greater carrier scattering at the adsorption surface. This observation is also supported by percentage gas molecule contributing to EG surface conductivity changes. Our result indicate that NH₃ contribute $0.01 \sim 0.1$ % while NO₂ contribute $1 \sim 2$ % for EG surface conductivity change. This observation is consistent with other amperometric measurement [29]. However, the novelty of this work is to separate out the scattering effect which coincides with the adsorption and gives the clear picture of conductivity change. Electronic transport in graphene is dominated primarily by two scattering mechanisms: 1) Shortrange scattering, and 2) Long-range coulomb scattering [31]. Short range scattering originates from short-range factors such as lattice defects and electronelectron interactions. Short range scattering potential give rise to a scattering time that varies as 1/E and independent of temperature. Long range scattering, on the other hand, originates from the screening of charged impurities on the surface of graphene. Fig. 4 shows both intra and interband scattering varies linearly with the impurity, attributes most likely to be long range scattering dominated.

Fig. 4. Scattering time as a function of impurity concentration.

Charge impurity scattering [32], For screened coulomb scattering that leads to a conductance which is proportional to $\sqrt{n_s}$. So, linear relation between conductance and $n_s n_s$ is the evidence of presence of charged impurity scattering. Our previous works [12] shows no significant contribution of intraband scattering because of no gas adsorbent molecule presence. With the adsorbent gas molecule n/ni significantly increases because of percentage charge transfer through the EG layer, supported by amperometric measurement, increases the charge impurity scattering, as a result interband scattering plays a dominant role which cannot be neglected even at DC.

5. Conclusion

In summary, we find that the infrared carrier transport in EG can be described only by accounting for the influence of interband scattering. In doing so, we find a self-consistent explanation of carrier transport in EG, where carrier scattering (interband and intraband) increases in response to surface impurities, along with a change in carrier concentration caused by charge transfer between the molecules and EG. This result was verified by an amperometric measurement also. This leads to an increase/decrease in overall conductivity/reflectivity depending on the tradeoff between scattering and carrier concentration. The most significant part of this study is that it gives us both carrier density and scattering (both intra and interband) considering the percentage charge transfer through the EG layer, attributes the doping concentration as well as overall conductivity change on EG films. This study is significantly important for EG sensing behavior as well as EG based FET devices.

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