GRAPHENE-BASED FLEXIBLE SENSORS: RECENT ADVANCES AND CHALLENGES

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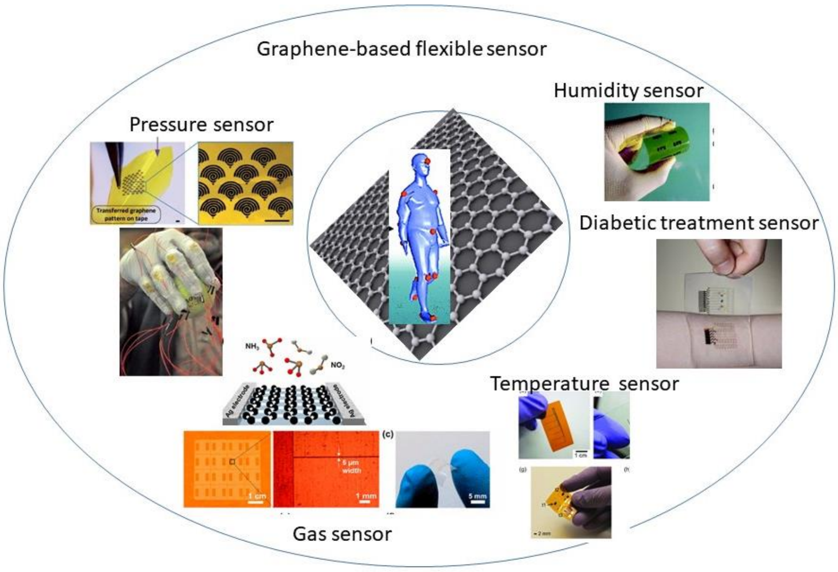
Abstract

Graphene based flexible sensor electronics have brought great interest in fabrication flexible electronic materials that offer both durability and high mechanical performance. These flexible wearable devices are used in a wide range of applications ranging from flexible display/transistors, smart sensors, energy harvest and storage, smart artificial sensing skins for robots, aircrafts, human machine interaction and epidermal electronics for healthcare applications. This pure project review focuses on the latest advances in flexible graphene based flexible transducer enabled fabrication strategies, materials and devices in combination with passive polymeric materials for electronic skin (E-skin) and electronic textiles (E-textile) applications.

1. Introduction

Graphene is a nanomaterial arranged in a two-dimensional layer of carbon atoms with sp^2 hybridization that are connected in a hexagonal lattice structure. Graphene has exceptional electrical, mechanical, and chemical properties. For example, it has high electron mobility, large surface area, high mechanical resistance, high flexibility, low weight, high thermal conductivity and can sustain extremely high electrical current densities (B.-T. Zhang, Zheng, Li, & Lin, 2013). Due to these excellent properties, it can be used in flexible electronic devices such as in sensors, batteries, supercapacitors, solar and fuel cells, and biotechnology. Furthermore, graphene and its derivatives such graphene oxide (GO)/reduced graphene oxide can also be used in flexible and stretchable sensors for wearable technology (Fig.1). For wearable gas, strain and biosensors, graphene can be very useful since its two-dimensional structure facilitates functionalization for the incorporation of biomolecules and nanoparticles and it has high biocompatibility. Developments in flexible electronics increase day by day and attracted more attention due to its common applied application such as products like smart watches. When the future of graphene nanomaterial enabled flexible electronics-based technologies and their potential application areas are considered, it is very important to consider latest development in flexible and stretchable electronic devices and skin. In this review, progress on graphene-based flexible gas, temperature, strain, pressure and bio/chemical (glucose and pH) sensors in terms of material preparation, sensor fabrication, and their performance are reviewed. The desired properties of these sensors such as sensitivity, selectivity, short response-recovery time, enduring high mechanical stress and strategies to operate at room temperature are also discussed and finally ends with future prospects and considerations of graphene based flexible and stretchable electronics for wearable technology.



Schematic 1: Schematic illustration of key applications of graphene based flexible and stretchable sensors that include gas, temperature, strain, pressure and bio/chemical (glucose and pH) sensors.

2. Graphene based flexible sensors

2.1 Graphene based flexible gas sensors

Reduced graphene oxide (RGO), synthesized by chemical reduction of exfoliated graphene oxide (GO), is a commonly used as sensing material in flexible gas sensors because of its large surface area, low signal-to-noise level, room temperature operation, and multifunctionality in chemical functionalization. To extent, it is mechanically flexible and environmentally stable. The availability of large-scale production and easiness of the composite fabrication compared to graphene (physical micromechanical cleavage or chemical vapor deposition (CVD) growth) intensifies the usage of RGO materials.

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Flexible gas sensors need to be highly sensitive and stable since they are very crucial parts of wearable electronic devices. (Park et al., 2018) fabricated a novel graphene fabric gas sensor composed of reduced graphene oxide (rGO) nanosheets and electrospun nylon-6 nanofibers. This study utilized rGO nanofibrous mesh fabrics (RGONMFs) NO_2 gas sensors which are highly flexible, mechanically stable, selective, and sensitive (Park et al., 2018). The RGONMFs were produced by dip-coating of GO nanosheets onto an electrospun nylon-6 nanofibrous mesh fabrics, then went under chemical reduction process. The RGONMF gas sensors kept their sensitivity and mechanical durability against repeated deformation tests which were consisting of 5000 bending cycles with an extreme bending radius of 1.0 mm (Fig.1). Furthermore, other than the high responsivity to NO_2 gas at room temperature, sensor was selective to some other gases such as formaldehyde, acetone, benzene, and ammonia. This flexible gas sensor is very promising for monitoring harmful gases in wearable flexible electronics.

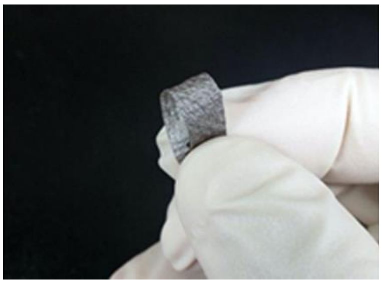

Figure 1- Photograph of a RGONMF(Park et al., 2018).

In order to fabricate flexible electrical gas sensors, recently attention has been drawn for fabrication of graphene films on flexible substrates. However, there are two major methods for that fabrication. One is based on gas-phase chemistry such as CVD, and the other is based on solution chemistry of which the graphene is mainly prepared by Hummer's method. The drawback is, these technologies require intensive work and they are not cost effective. Nevertheless, mentioned drawbacks can be overcome. Recently chen et al. (Chen, Liu, Lin, & Wu, 2019) proposed electrochemical-assisted deposition (ECAD) method in order to deposit GO on poly-ethylene terephthalate (PET) substrate patterned with interdigitated electrodes (IDEs). Electrical force was used to drive GO sheets to electrodes and then GO film is turned into RGO film in hydrazine vapor and bridged the IDEs on PET substrate. Fig.3 (c-d) showing SEM images of difference caused by ECAD process. This process yielded homogeneous film with good ohmic connection to IDEs with low noise and suitable resistance. ECAD graphene film is very less costly than CVD and transferring process. To extent, it demonstrated very high gas sensitivity performance to isoprene gas at room temperature. Furthermore, reported graphene nano-sensor can be applicated for non-planar sensing cases, especially for complex geometric objects. For example, paper-based gas sensor can be affected from humidity and its' micro-morphology can be altered. However, RGO are not affected and that emphasizes the importance of deposition of RGO on polymer substrate for constructing flexible sensors. For application, this sensor can be used in food quality monitoring. In order to test that, (Chen et al., 2019) conducted experiments and measured odor emission of different fruits in different maturity stages (Fig.2). The results were very satisfactory, it is observed that it can trace the fruit maturity. So, it shows that, ECAD method is very promising for preparing flexible graphene devices. This sensor can be further incorporated to skin, plants or food and it can be used for medical applications such as chronic disease monitoring and disease screening.

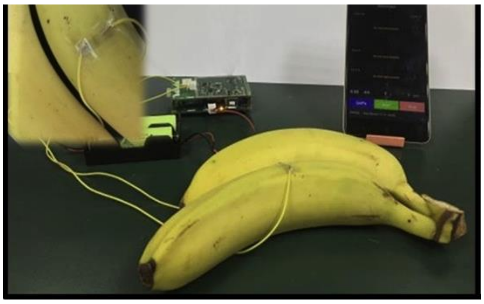

Figure 2-The sensing modules for surveillance of food quality(Chen et al., 2019).

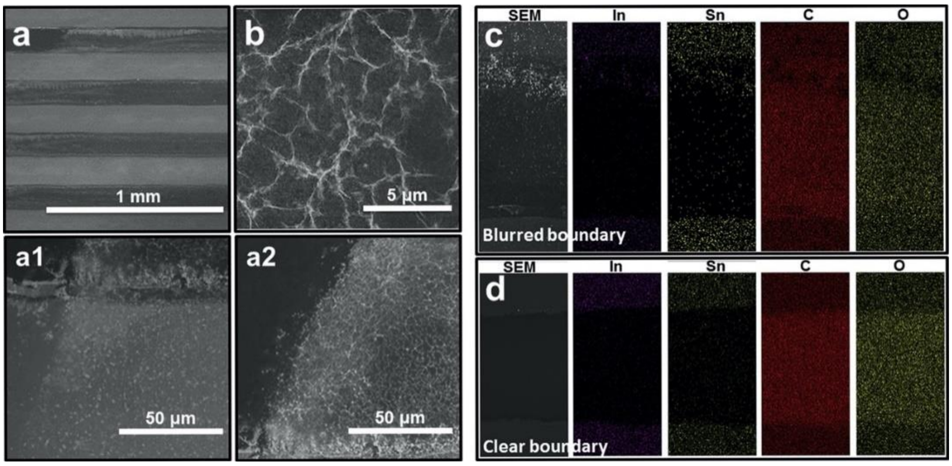

Figure 3- SEM image and EDS (Energy Dispersion Spectroscopy) mapping of a typical rGO@ITO (indium tin oxide)-PET by ECAD. (a) An overview of rGO@ITO-PET, (a1) and (a2) are the morphologies of graphene networks on the electrodes and between the electrodes, respectively, and (b) is the zoom in SEM image of graphene networks between the electrodes. (c) and (d) are EDS mappings between the adjacent electrodes with and without ECAD process, respectively(Chen et al., 2019).

The detection of NO_2 gas is an important issue because it is damages soil when it is somehow exposure to it. Then it affects plants, animals, and human health after some time. NO_2 can be produced by the burning of fuel, car exhaust or industrial production processes. There are some options for NO2 detecting sensors such as solid-state NO_2 sensors. Even though they have low cost and high sensitivity, they can only operate in high temperatures. Also, they are very power consuming, unstable and unselective. That is why sensors with fast response- recovery time, sensitive, inexpensive and suitable to be operated in room temperature are some of the desired properties. Graphene based composites enable us to have these properties. Recently, Chavez et al. (Chavez et al., 2021) produced flexible graphene composites (FGCs) decorated with V_2O_5 (VO) microbelts and used them as gas sensors for NO_2 detection. In order to fabricate a flexible graphene sensor for NO_2 detection, they used VO microbelts as active material of the sensor (Fig.4a-b). Because of the existence of reactive oxygen species such as O_2 and O on the surface of VO particles, they enabled the adsorption of NO_2 molecules. The best response/recovery times measured were 19/26 s, respectively. However, the flexible sensors were saturated and incapable of detecting NO_2 after 4–17 cycles of use, but their detection was recovered when the sensor was exposure to UV light. Also, this gas sensor demonstrates high selectivity and it is cost effective since it responded to only NO_2 in presence of CO_2. The fabricated sensor in this study decrease in the operating temperature and response/recovery times of VO based NO_2 sensors (Chavez et al., 2021). The presence of VO enabled them to detect NO_2 in a very sensitive way at room temperature. Since this sensor is flexible, conductive and it has porous structure, it can inspire the researches in new flexible gas sensors.

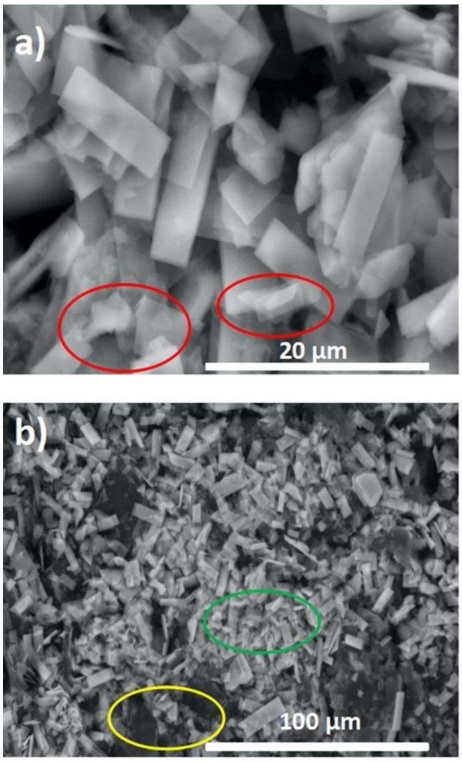

Figure 4- SEM images of: a) VO microbelts and b) FGVO composite (FGC+VO=FGVO composite) (Chavez et al., 2021).

Further, laser induced graphene (LIG) is a good method to synthesis porous graphene in a simple, easier and quicker manner. Because as mentioned before, graphene is hard to be produced directly in large scale. Therefore, Stanford et al. (Stanford, Yang, Chyan, Kittrell, & Tour, 2019) fabricated gas sensors by lasing polyimide (PI) substrates with a 10.6 µm CO_2 laser, and acquired 3D porous graphene (Fig.5). This method showed promise to fabricate flexible gas sensors in large scale which have the capability of detecting wide range of gases based on their thermal conductivities and it can be called as thermal conductivity detectors as well (TCD). Due to graphene's high surface area to volume ratio and high conductivity, its properties can be altered by the chemical absorption of the gases. By detecting these changes, identification of gases with high degree of precision was possible. The fabricated sensor demonstrated detection of gases such as SO_2, H_2, NO_2 and NH_3 with fast response times of 7-8 s.. The fast response ability is owed to large surface are and high thermal conductivity of LIG. Additionally, the power consumption for these devices (~28 mW) is low in comparison to other micro-thermal conductivity detectors. Because of 3D porous structure, these sensors are flexible. Flexibility permits gas sensors to be easily transferred to other matrices by a transfer process and makes them suitable for incorporation in various different surfaces and to be used in different applications for instance, LIG microstructures can be used in supercapacitors, wearable sensors. However, the limitation factor in this type of sensor is caused by the time passing until the gas introduces with the chamber that may affect the sensitivity and response of the sensor.

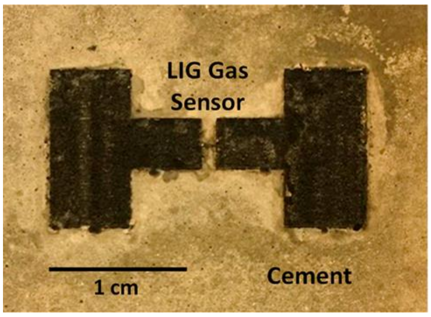

Figure 5- Optical image of the LIG sensor-embedded in cement. (Stanford et al., 2019)

Ammonia (NH_3) gas has a wide usage in several production processes. However, it is very dangerous for the human health. It can cause some complications such as asthma, cough etc. That is why it is significant to detect this invisible gas in order to prevent some accidents. Due to these possible threats, flexible gas sensors which can operate in room temperature, endurable to high strain, that have great sensitivity and show low rates of energy consumption became the matter of consideration. For this application, reduced graphene oxide (rGO) is a great option for gas detection because its electrical properties can be arranged according to graphene oxide's (GO) reduction level. However, it has some drawbacks such as poor selectivity. Therefore, rGO is decorated with metal oxides, such as SnO_2, ZnO, TiO_2 in order to improve selectivity and arrange the electronic structure.

$Ti_3C_2T_x$ MXene is a recently developed class of 2D material, they have configuration of $M_{n+1}X_nT_x$, in which M, X, and T represent a transition metal, carbon/nitrogen, and surface terminal functionalities such as O, F, and OH, respectively. These functional groups act as active sites for adsorption, reinforce the charge transfer and contribute to the adsorption of NH_3, which makes MXene highy selective for NH_3 gas in room temperature. However, narrow band gap property of MXene causes low gas response.

Lately, It was reported that graphene fibers (GFs) can be fabricated by the wet- spinning of a highly concentrated GO dispersion. Since GFs are fibrous structures, flexible, and lightweight; they are highly advantageous for wearable gas-sensing applications. Lee et al. (Lee et al., 2020) constructed a strategy to fabricate hybrid fibers consisting of layers of Ti C T MXene and GO sheets through a scalable one-step wet-spinning process. In order to prevent any damage to fibrous structure, they incorporated an organic solvent system to avoid the use of additives (Fig.6). This method enables MXene/GO fiber to endure continuous tensile even after bending over 2000 cycles. MXene/rGO hybrid fibers demonstrated excellent NH_3 sensing response ($\Delta R/R_0$ = 6.77%), low power consumption, excellent flexibility and stability to mechanical deformation, making them a very promising material for wearable-flexible sensing devices. For example, flexible MXene/graphene hybrid fibers were used in the textile of a lab coat and yielded reliable sensing results and proved its high potential for wearable devices. This method can also be used in production of portable-wearable energy devices. Table 1 summarized recent advanced on graphene based flexible gas sensors with composition parameters and applications.

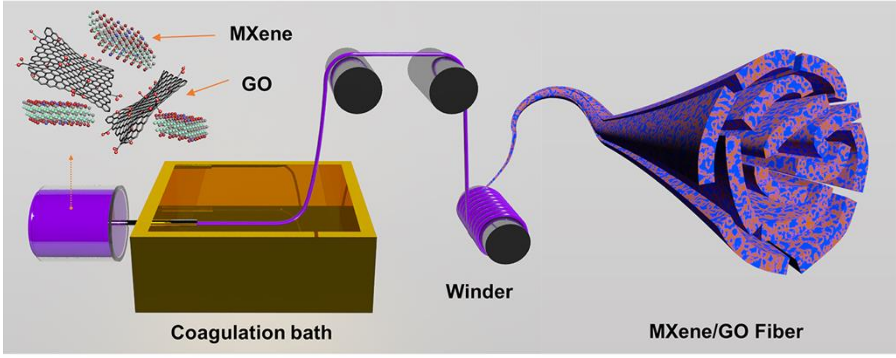

Figure 6- Schematic illustration of the spinning process for MXene/GO hybrid fiber (Lee et al., 2020).

Table 1: Graphene based flexible gas sensor with composition and detectable gases and applications.

Gas Sensors			
Owner of the Work	Composition of the Sensor	Detection Ability	Application
(Park, Kim et al. 2018)	rGO nanosheets and nylon-6 nanofibers	NO2 detection especially	monitoring harmful gases
(Chen, Liu et al. 2019)	rGO on PET patterned with IDE's	isoprene and hydrothion were tested	food quality monitoring
(Chavez, Gomez-Solis et al. 2021)	flexible graphene composite decorated with V2O5	NO2 detection	wearable sensors
(Stanford, Yang et al. 2019)	LIG on PI substrate	detection of wide range of gases (SO2, H2…)	wearable sensors, supercapacitors
(Lee, Eom et al. 2020)	MXene layers and GO fibers	NH3 detection	wearable devices

2.2 Graphene based flexible humidity sensors

Humidity sensors are widely used in several measurements and in lots of industrial processes. Therefore, accurate, precise measurement of humidity gained much importance recently. Additionally, a high- performance humidity sensor must meet many requirements, such as linear response, high sensitivity, fast response time, chemical and physical stability, wide operating range of humidity and low cost.

Respiration is one of the most important physiologic indicators which needs to be monitored carefully in order to understand the health conditions thoroughly. It can be used for diagnosis of diseases and identifying various risks related to the cardiovascular problems. Respiration can be monitored by detecting humidity within breathe. In order to fabricate flexible humidity sensors, several ductile materials are used as substrates. Some of them are polyethylene terephthalate (PET), and paper. However, polymer film-based sensors have limited tendency to absorb moisture, which causes a reduction in their sensitivity and comfort. Paper-based sensors have some drawbacks such as being fragile. Recently, textiles have been used as a material for the fabrication of wearable flexible electronic devices, such as biosensors. Since textiles are tendent to absorb moisture, have breathable and soft structure; they can be easily incorporated in clothes.

GO contains various reactive oxygen functional groups, such as epoxy, hydroxyl and carboxyl groups, which make it highly hydrophilic, moisture-sensitive and perfect for humidity- sensing materials. Furthermore, Bovine serum albumin (BSA), an amphiphilic protein, can be attached to both organic and inorganic materials in order to facilitate the adsorption of GO onto textiles. Hence, BSA as an adhesion agent is reliable for e-textiles, but it has not yet been applied to humidity sensors until Wang's et al. (Yamei Wang, Zhang, Zhang, Sun, & Chen, 2020) reported work. They reported a GO/nonwoven fabric (NWF) based flexible and wearable humidity sensor for real-time respiration monitoring. BSA was added to improve the adsorption of GO onto the NWF with interdigital electrodes (IDE) fabricated by magnetron sputtering (Fig7a-g). The resulting humidity sensor was highly sensitive, able to give fast response. The optimal concentration of BSA was 2 wt %, which was the value that sensor obtained the shortest average response time (~8.9 s) and recovery time (~11.76 s) to achieve high sensitivity. This sensor was especially used to detect human respiration and identifying different types of breathing. This shows that GO/ NWF humidity sensor has a potential to be used in human healthcare for various purposes such as monitoring physiologic activities by being integrated to masks etc.

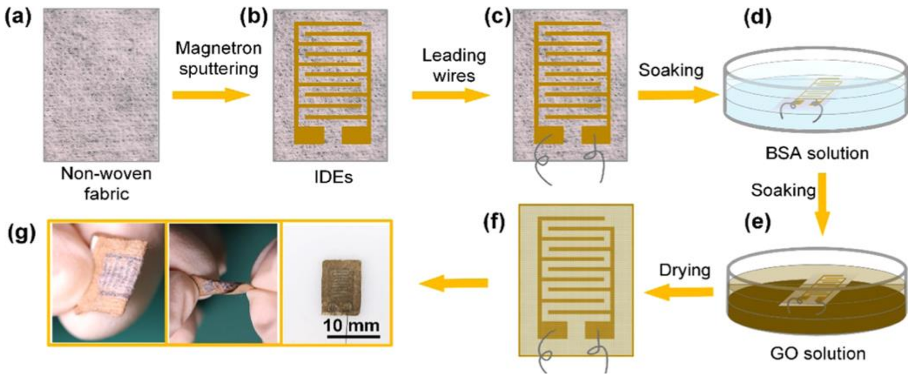

Figure 7- Schematic of the device fabrication process (a−g) (Yamei Wang et al., 2020).

As mentioned before, GO is not conductive as graphene and this can be improved by reduction process of GO. That is why, reduced graphene oxide (rGO) is a good alternative for gas sensors with both conductivity and chemically active defect sites. However, when compared with graphene, multilayered rGO has low surface area to sense the gas, which decreases the sensors' sensitivity. Gu et al. (Guo et al., 2012) fabricated a humidity sensor by using graphene oxide on flexible polyethylene terephthalate (PET) substrates. In order to increase the performance of its sensing properties, two-beam-laser interference (TBLI) is used for GO reduction (Fig.8). They produce hierarchical rGO nanostructures. These nanostructures increase the surface area and the arrangement in oxygen groups enables them to control adsorption behavior of water molecules. Thus, reduction process increases the materials ability to adsorb outside molecules and therefore provides higher performance for sensing. Also, they tune the laser power and observe how it affects the content of oxygen functional groups in GO-they remove oxygen functional groups-, which eventually affects the conductivity of rGO. Hence, TBLI fabrication of RGO increases the sensitivity to humidity at room temperature and yield faster response-recovery time for the humidity sensor. Since this reported fabrication method is mask-free, surfactant-free and large-scaled, it is very promising for production of nanostructured graphene based microdevices.

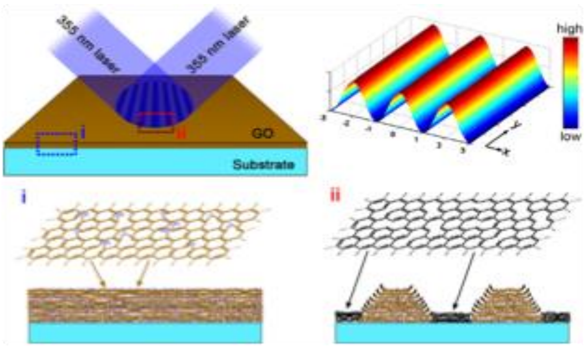

Figure 8- Illustration of TBLI reduction of GO film (Guo et al., 2012).

Chi et al. (Chi, Ze, Zhou, & Wang, 2021) explored different applications of GO on different substrates for colorimetric humidity sensor. These substrates were aluminum foil (Al), silicon and metallized polyethylene terephthalate (mPET). Factors that affect reflectance spectra of GO films are found to be dispersing solvent, substrates, concentration and pulling speed of substrates during dip-coating. Results indicated that GO film on silicon substrate from 1.6 wt% acetone solution with a pulling rate of 150 mm/min showed a better spectra resolution and humidity response within the visible range under all humidity environment. While GO film fabricated from 2.4 wt% acetone solution on mPET film with pulling rate of 100 mm/min showed distinguishable peak intensity and improved humidity detection (Fig.9). They realized that fabricating it from acetone dispersion instead of aqueous dispersion showed better spectra resolution, better surface energy matching, higher color contrast, enhanced its sensitivity and provided faster film formation process. The sensor signal was interpreted as function of change in wavelength and color change as shown in Fig.10 a-d for the humidity sensing from RH 0 to 96%. Also, bending test of GO film on mPET demonstrated an excellent stability and endured upon 10,000 cycles of bending, which indicates that these devices are very promising to be used in flexible device applications for monitoring physiological conditions or environmental condition change detections. Since wearable humid sensors are getting widely common with the usage of Apple watch, Google Glass etc. this sensor can be used to measure and record individuals' physiological information such as sweating rate, respiration rate, calories burned and monitoring individuals' health by being used for some diagnostic purposes. This method does not require any outside electrical source in order to sense the humidity level. That makes it very cost effective as well. Also, it has easier fabrication process when compared to other alternatives. Due to these properties, this sensor can be used as a disposable humidity sensor which can be incorporated in food packages, dry boxes etc.

Figure 9- Photograph of the aGO-mPET 100 on the bending machine. The sample was prepared with 2.4 wt% GO solution by pulling rate of 100 mm/min (Chi et al., 2021).

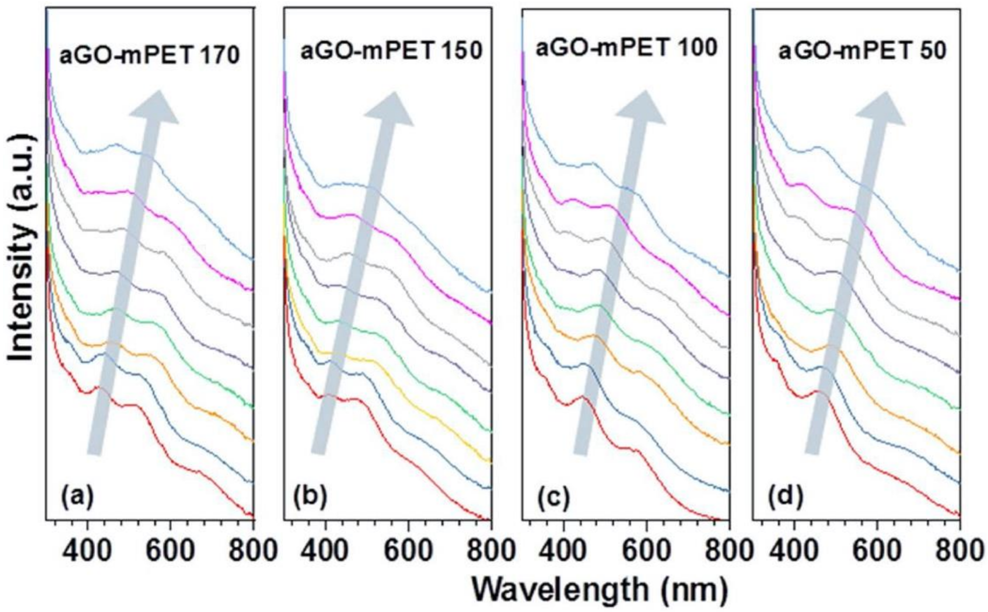

Figure 10- Moisture (RH = 0%, 12%, 33%, 44%, 55%, 68%, 75% and 96%) response of the 2.4 wt% acetone dispersed GOs on mPET with different pulling rate (a) 170 mm/min, (b) 150 mm/min, (c) 100 mm/min and (d) 50 mm/min (Chi et al., 2021).

Su et al. (Su, Shiu, & Tsai, 2015) reported development of flexible impedance-type humidity sensors. For this, Au nanoparticles (AuNPs), GO, hydrolyzed mercaptopropyltrimethoxysilane (MPTMOS) sol–gel films are fabricated on a polyethylene terephthalate (PET) substrate. These sensors were fabricated by two processes: self-assembly and the sol–gel technique. Sol–gel is a technique used to fabricate porous structure composed of transition metal alkoxides. Self-assembly is a popular method to acquire modified surfaces with desired properties. It is simple, cost-effective, provides homogenous product and it has high degree of organization. The production process is about dropping MPTMOS sol–gel solution that contains GO on to the surface of Au electrodes which are on PET substrate, and then AuNPs were assembled onto the thiol groups of the sol–gel network (Fig.11). Since graphene is highly mechanically strong, flexible, low cost, has great surface area and permits the electron transfer at room temperature, it is preferred for many sensing devices and introducing GO increased the flexibility of the AuNPs/GO/MPTMOS sol–gel film. Although the functional groups such as hydroxyl, epoxide and carboxyl groups are responsible for the high hydrophilicity of GO, they also cause electrical insulation. However, self-assembly of AuNPs on the silica gel provided some conduction pathways and improved the conductivity, thus improved the sensitivity and linearity of the sensing film. The sensor which demonstrated the greatest flexibility, sensitivity, linearity and long-term stability was made from the AuNPs/GO/MPTMOS sol–gel film with 9.0 wt% added GO. The response time and recovery time of the sensor were 119 and 125 s. The linearity of the humidity sensor was dependent on the applied frequency.

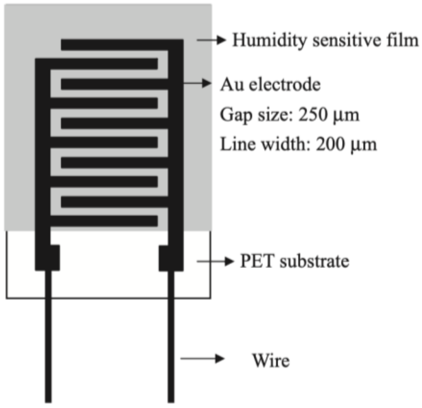

Figure 11- Structure of humidity sensor (Su et al., 2015).

Lan et al. (Lan et al., 2020) suggested laser-induced graphene (LIG) with a porous structure as an efficiently active material for flexible electrodes. It is obtained by a laser direct writing technology on polymer surface under an ambient atmosphere (Fig.12). As implied before, effective approach for massive production of flexible capacitive-type humidity sensor is possible. To augment the sensing performance of the humidity sensor GO was introduced because of its distinctive 2D structure. The GO-based humidity sensor is very flexible, sensitive and long-term stable. Sensitivity of the humidity sensor increases with the increase of GO concentration on the sensor. However, the response time of the sensor is dependent on GO and increases with its amount. The response time is approximately 15.8 s between 20% relative humidity (RH) and 80% RH. This humidity sensor also exhibits low hysteresis during the changes in relative humidity which implies that it can be used under high humidity conditions. Since flexibility is very significant for the wearable applications, the capacitance change of the sensor was almost negligible after it was bent with different angles. That means it can be very well used for this purpose. Moreover, again, its capacitance showed negligible variation with time which proves the long-term stability of this GO- based humidity sensor.

This GO-based humidity sensor can be used for monitoring human activities. For example, it can be integrated to a mask for monitoring human respiration. Furthermore, it can be used in agricultural area. In order to detect the agricultural output, measuring the humidity level that affects the plants' growth rate, photosynthesis rate is important. Until now, the proposed methods to monitor water status of plants was using sensors that are fixed on leaves. However, these sensors were mechanically rigid and incompatible for the soft surface of plant leaves. Recently Lan et al. (Lan et al., 2020) fabricated GO based humidity sensor allows us to detect humidity without damaging the leaves. Table 2 summarized recent advanced on graphene based flexible humidity sensors with composition parameters and applications.

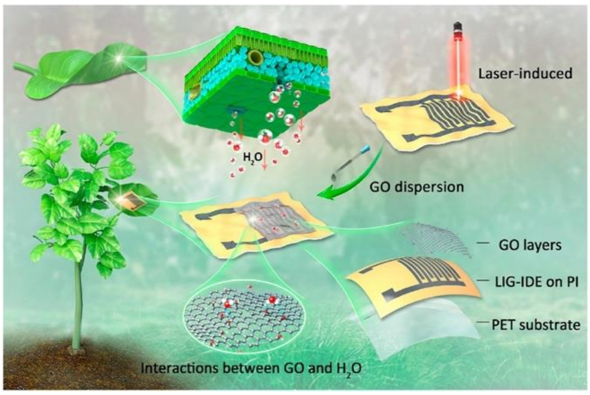

Figure 12- Schematic illustration of the fabrication process of the flexible humidity sensor that can detect humidity of leaves (Lan et al., 2020).

Table 2: Graphene based flexible humidity sensors with composition parameters and applications.

Humidity Sensors		
Owner of the Work	Composition of the Sensor	Application
(Wang, Zhang et al. 2020)	GO, Bovine Serum Albumin	monitoring human respiration
(Guo, Jiang et al. 2012)	rGO on PET substrate	nanostructured microdevices
(Chi, Ze et al. 2021)	GO film on Si and mPET	food packages, wearable sensors
(Su, Shiu et al. 2015)	AuNP's, GO, MPTMOS sol-gel films on PET substrate	wearable sensors
(Lan, Le et al. 2020)	Graphene Oxide	agricultural area, monitoring human activities

3. Graphene based flexible temperature sensors

Graphene is widely used in wearable devices due to its properties such as high mobility, outstanding thermal conductivity, transparency, biocompatibility, flexibility. Monolayer graphene was used as a thermal sensitive element using conventional micro-nanofabrication techniques on silicone substrate of temperature sensor but it had a problem of low flexibility. According to report by Yetisen et al. (Yetisen et al. 2016), there are many parameters that define the sensitivity and performance of a temperature sensor. Thermal resistance of a material can be defined as the ratio of the temperature difference between two faces of the material to the rate of heat flow per unit area. Therefore, if thermal resistance of sensor is higher that it will lead the heat loss lower. Also there is a term called temperature coefficient of resistance (TCR) which means the average slope of the resistance values in a temperature range. Temperature sensors exhibit thermistor, photoelectric and thermoelectric effects during measurement of human body temperature. There are two types of thermistors: positive temperature coefficient (PTC), which increases when temperature increases and negative temperature coefficient (NTC), which decreases when temperature increases. The temperature sensitivity of graphene and its derivative (GO/rGO) based sensor is crucial to measure spatial skin temperature, for example 5 °C variations across a 1-cm-wide ulcer. RGO wearable sensors provide temperature measurement of topographically complex plantar surface in a conformal, intimate, comfortable and breathable way. These characteristics can be used in smart health applications such as monitoring chronic wound healing, projecting ovulation cycles, detecting sleepiness and anxiety… Some other examples are cardiovascular diseases can weaken blood circulation and lower ankles' and toes' skin temperature, emotional feelings are correlated with skin temperature too that happiness makes the body warm but sadness makes arms and legs cooler.

Vuorined et al. (Vuorinen et al. 2016) fabricated temperature sensors based on inkjet printed graphene-PEDOT:PSS(poly polystyrene sulfonate) composite with a polyurethane plaster (Fig.13). It had a good adhesion with the skin and TCR value was approximately 0.06% $°C^{-1}$ under 35-45°C. Ambient atmosphere had some impacts on this non-capsulated device that different gases changed the temperature resistance values but also these impacts can be reduced by using a fluoropolymer coating. The completed sensor is light-weighted, thin and integrate with the skin well. Although development process of this sensor was not finished, the present form can be used as a fever indicator in human skin.

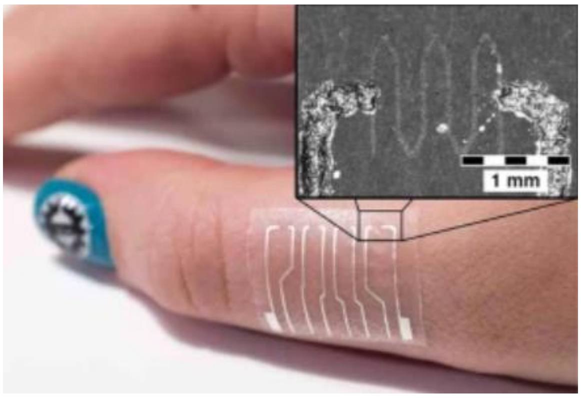

Figure 13 – inkjet printed graphene-PEDOT:PSS temperature sensor (Vuorinen et al. 2016).

Hilal et al. (Hilal et al. 2020) fabricated temperature sensor by utilizing PET(Polyethylene terephthalate) fiber with Ni and graphene as sensing element. Fir this, a uniform film of Ni over PET by using simple rotating device inside the sputtering chamber and finally in order to create adhesion between graphene and Ni-PET fiber, microstructure were created on the central part of Ni which was followed by the process of heating at 100 °C for 30 min inside the vacuum oven. They obtained maximum TCR of 1.5×10‒3 (°C^{-1}) but when they used graphene over Ni/PET fiber as temperature sensor, 7.10 times higher TCR was achieved compared to without graphene sensor. Also, the linear response was achieved by graphene/Ni-based temperature sensor for TCR curve after 10,000 bending tests. Also, when the humidity changed between %40 and %90 its TCR did not change, also TCR was stable at 3.90 KΩ upon replacing O_2 gas with N_2 gas. It was observed that when sensor was exposed to diverse alcoholic environments such as acetone, isopropyl alcohol, methanol and ethanol for 20 minutes, the TCR of the sensor also stayed stable at 3.90 KΩ (Fig. 14).

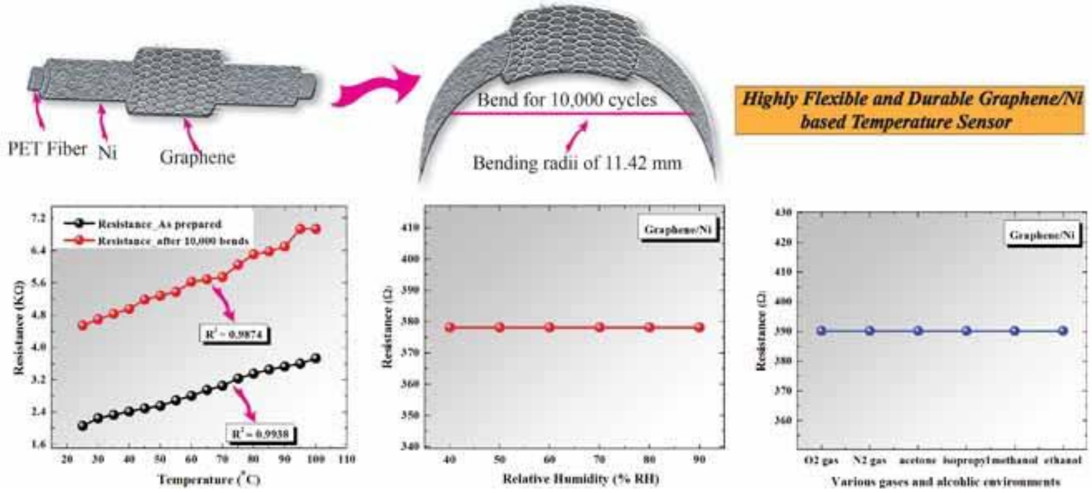

Figure 14 – (a) Resistance-Temperature graph (b) Resistance-Humidity graph and (c) Resistance-Various gases and alcoholic environment graph (Hilal & Han, 2020).

GNWs are good candidates for temperature sensors because they are highly sensitive, stable and flexible temperature responsive material. Graphene nanowalls (GNWs) were used to fabricate temperature sensor(Lu, Yang, & Liu, 2020; Yang et al., 2015). GNWs has a property of being highly stretchable because vertically aligned graphene nanowalls to be interlaced as distinguished from graphene and as result this property increase temperature sensitivity.

Yang et al. fabricated temperature sensors based on GNWs/PDMS using plasma enhanced chemical vapor deposition technique and polymer-assisted transfer method. In this study, TCR was achieved up to 0.214 °C^{-1}, which is three times higher than conventional temperature sensors. On optical and atomic force microscopy used to observe the morphology change of GNWs/PDMS sensor and it was shown such high response of it was caused by the excellent stretch-ability of GNWs and large expansion coefficient of PDMS (Fig.15). It was shown that GNWs/PDMS temperature sensors was suitable for human body's temperature and responses are very fast and can be used in different areas like flexible electronics, human health monitoring, human machine interface.

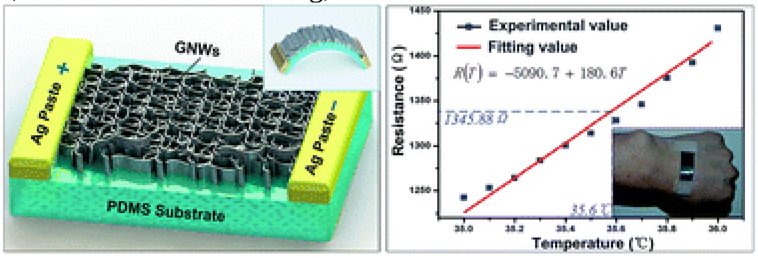

Figure 15 – a) GNWs/Ag temperature sensor on PDMS substrate and b) Resistance-Temperature curve response of GNWs/PDMS temperature sensor (Yang et al., 2015).

Boon et al (Boon, 2017). developed GO based temperature sensor. In this work, graphene-oxide(GO) was synthesized by using Hummers method and then used thermal reduction at 250°C for 12 h under ambient atmosphere to produced reduced graphene-oxide (rGO). Inkjet printing was used to integrate rGO with polyimide substrate as shown in. This rGO based temperature sensor was used to resolve skin temperature (around 0.7°C) of human foot – between metatarsal and medial arch locations and conformal nature of rGO made it sufficient for topographically complex and moving skin surface. The mechanism of the fabricate temperature sensor was correlated to three possible mechanisms: (a) thermally activated electron transfer between graphene sheets, (b) functional groups acting as ionic charge carriers and (c) hopping of charge carriers from pristine graphitic region to pristine graphitic disordered region. The electrons which are delocalized over the pristine regions must cross over–hop-the defective regions in order for the sensor to be conductive. These hopping across defective regions is mostly dependent on temperature and energy available for those electrons. Temperature sensitivity is mainly dependent on the size and number of the defective regions of rGO. The sensitivity of the sensor was reported between 0-150°C which may work in body temperature (physiological temperature). It is foreseen that rGO temperature sensors can be used to see spatiotemporal plantar temperature changes correlated with the healing of foot ulcer caused by diabetes.

Yu et al. used (Yu, Yu, & Dai, 2020), graphene fibers sensing material to solve strain sensitivity problem in wearable temperature sensors. They used sandwich structure design with two-sided temperature sensor with graphene and SiO_2. Polyamic acid(PAA) with a mass fraction of 12wt% was used as a support layer on top of the SiO_2 by spin-coating method (Fig.16). Responsivity of this sensor was around 0.85% $°C^{-1}$ and sensing resolution was 0.1°C with a response time of 11.2 s between the range of 20-30°C. It also had good anti-interference ability in normal bending and axial stretching and below 90% tensile strain or a curved surface with a curvature of 0.5.

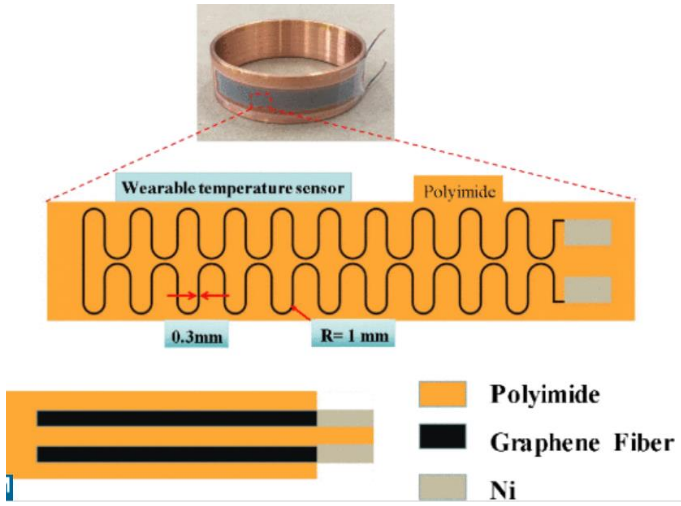

Figure 16 - Photograph and structure diagram of wearable temperature sensor (Yu, M., et al. 2020).

There are two methods to minimize strain interference in wearable temperature sensors (Yu et al., 2020). First one is to use a special fractal design to change the spatial structure of graphene (coiled shapes, serpentine patterns, pixel-like arrays) to reduce strain sensitivity. Second one is using post-compensation. These two methods have negative sides too, first method – using special fractal design-often increase the complexity of the process and large-scale production gets harder. Post-compensation causes the sensor system to become more complicated and it limits the simplicity of sensor and being lightweight.

In another study of (Jin, Y., et al. 2018), reduced graphene oxide was used as a temperature sensitive element in a textile-infused temperature sensor array because of its negative temperature coefficient property (Fig.17). Nylon filaments were coated with rGO and stitched with Ag into a polyester fabric to create the array of 6x6 NTC sensing elements. This rGO film was fabricated by inkjet-printing and chemical reduction. The rGO film remained mechanically and electrically stable when stretching (<4% strain) and bending (<34°). This sensor exhibited stretch-ability to 4% strain which is quite impressive in comparison with all other temperature sensing materials (i.e., metals and ceramics). Further, this temperature sensor was compared to infrared imaging and the accuracy of the sensor was enough to be comparable to infrared cameras.

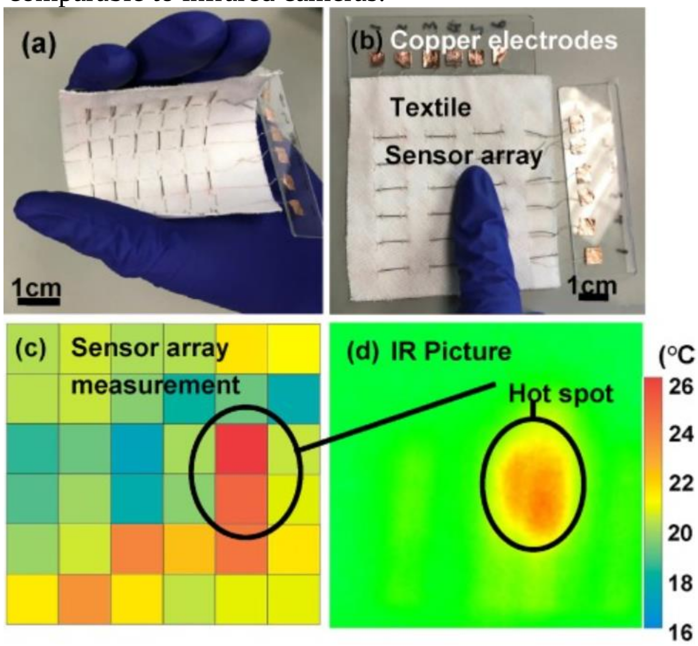

Figure 17 - (a) Optical image of the textile-infused array of 6 × 6 temperature sensors. (b) The sensor array touched by a thumb to generate the temperature distribution measured by (c) the sensor array and (d) an IR camera based temperature measurement (Jin, Y., et al. 2018).

There were also some difficulties while producing these rGO based temperature sensors that it was difficult to keep consistent electrical connections between Ag and rGO while stretching and bending occurs. This may be solved by mechanically conformal and electrically conductive polymeric bonding materials such as polyaniline and polypyrole. Another difficulty is the weak bond between individual rGO sheets –Van der Waals forces – may cause mechanical instability of rGO films under high level of strain. These forces are very dependent on the distance between adjacent sheets. To solve this problem, Lu et al. (Lu, L., et al. 2020) developed multifunctional sensor of graphite nanosheet (GN)/polyamide 66 (PA66) nanofibers composite which was prepared by electrospinning fibrous mat process and ultrasonic decoration method. In order to test thermal properties of this sensor, first repeatability test was done that the sample was placed at the hot plate with temperature of 100 °C and temperature of 30 °C for 100 cycles. Also hot wind at 100 °C was applied to sensor for testing and in another testing flexible sensor was put to human finger and finger was put in hot water. After these testings, it was demonstrated that this sensor has very quick and precise response and GN guarantees god heat transfer effect. Also, the figure below shows the resistance variation against temperature from 30 to 130 °C, and NTC effect of resistance is observed (Fig.18). It was foreseen that these multifunctional sensors can be used for physiological ECG, soft robotics, electronic skin and thermal protection applications.

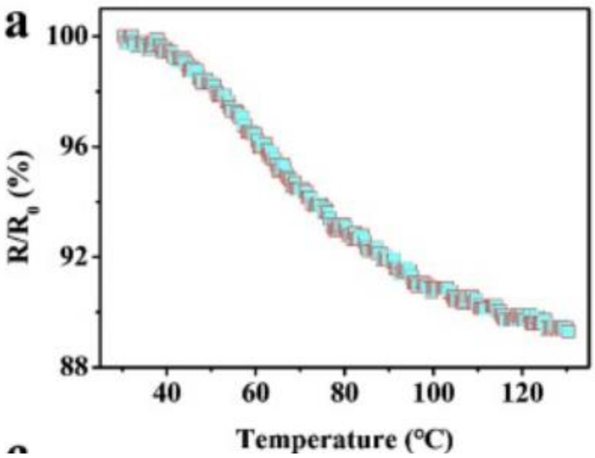

Figure 18 - (a) The resistance–temperature curve from 30 to 130 °C (Lu, L., et al. 2020).

Xie et al. (Xie et al., 2017) reported a flexible thermoelectric nanogenerator (TENG) composed of MoS_2/graphene nanocomposite. They prepared MoS_2 nanomaterials by a hydrothermal process, an indium tin oxide (ITO)-coated PET sheet was used as substrate. MoS_2/graphene nanocomposite was prepared by sonication and then PEDOT:PSS was added in it. This mixture was coated onto ITO/PET substrate. Also, silver paste was used as the top conductive electrode of the device. It has enhanced thermoelectric performance compared to bare MoS_2 nanomaterials probably because of graphene to work as a charge transfer channel in the composite and increase electrical conductivity. Under temperature difference of -35K, the MoS_2/graphene TENG generate an output voltage of -0.73mV, but pure MoS_2 TENG and pure graphene TENG can only generate 1/8 of it. This nanogenerator can be applied as a self-powered sensor for temperature measurements and it is beneficial for harvesting environmental thermal energy. By attaching this flexible TENG onto a glass bottle, it can harvest the wasted heat and then can be used as a self-powered temperature sensor as shown in (Fig.19). Graphene based flexible sensors with composition parameters and applications are summarized in Table 3.

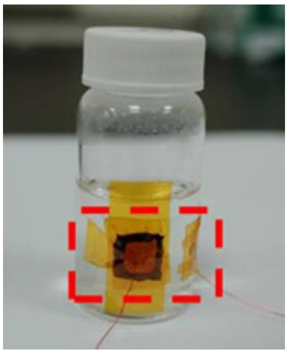

Figure 19 – TENG shown on a glass bottle for as a self-powered temperature sensor (Xie, Y., et al. 2017).

Table 3: Graphene based flexible sensors with composition parameters and applications

Owner of the Work	**Composition of the Sensor**	**Application**
(Vuorinen et al. 2016)	graphene-PEDOT:PSS composite with a polyurethane	fever indicator
(Hilal et al. 2020)	Ni/Graphene on PET fiber	wearable devices in different environments

(Yang et al. 2015)	GNWs on PDMS	human health monitoring, human machine interface…
(Boon et al. 2017)	rGO on Polyimide	detecting foot ulcer caused by diabetes
(Yu, M., et al. 2020)	Graphene fibers on SiO_2 with PAA	Anti-strain interference human body temperature monitoring
(Jin, Y., et al. 2018)	rGO/Ag on Nylon filaments	monitoring chronic wound healing, projecting ovulation cycles, detecting sleepiness and anxiety
(Lu, L., et al. 2020)	graphite nanosheet(GN)/polyamide 66 (PA66) nanofibers composite	physiological ECG, soft robotics, electronic skin, thermal protection
(Xie, Y., et al. 2017)	MoS_2/graphene nanocomposite with PEDOT:PSS on ITO/PET substrate	harvest wasted heat on glass bottle and self-powering

4. Graphene based flexible strain & pressure sensors

Graphene is one of the most beneficial matters used in a lot of nanotechnological development. Graphene is the suitable choice as sensing materials for strain and pressure sensors due to excellent electrical and mechanical properties (Zewei et al., 2019). Graphene possess high electrical conductivity as a results graphene and its derivatives have been frequently used to fabricate conducting layer or electrodes in the development of flexible strain and pressure sensors. Recently, many reports showed that graphene exhibited highest sensitivities in flexible pressure sensor device fabrication. On the other hand, graphene based flexible strain sensors exhibit highest gauge factor. Strain and pressure sensors can be classified in three types based on their transducing mechanism that include resistive sensor, capacitive sensor and piezo-resistive sensor (Fig.20). These sensors have a wide range of potential applications such as health monitoring, human motion detector, device system interaction, human-machine interaction and artificial intelligence. In the following section, brief information on resistive sensor, capacitive sensor and piezo-resistive sensor with functions and characteristic parameters are described.

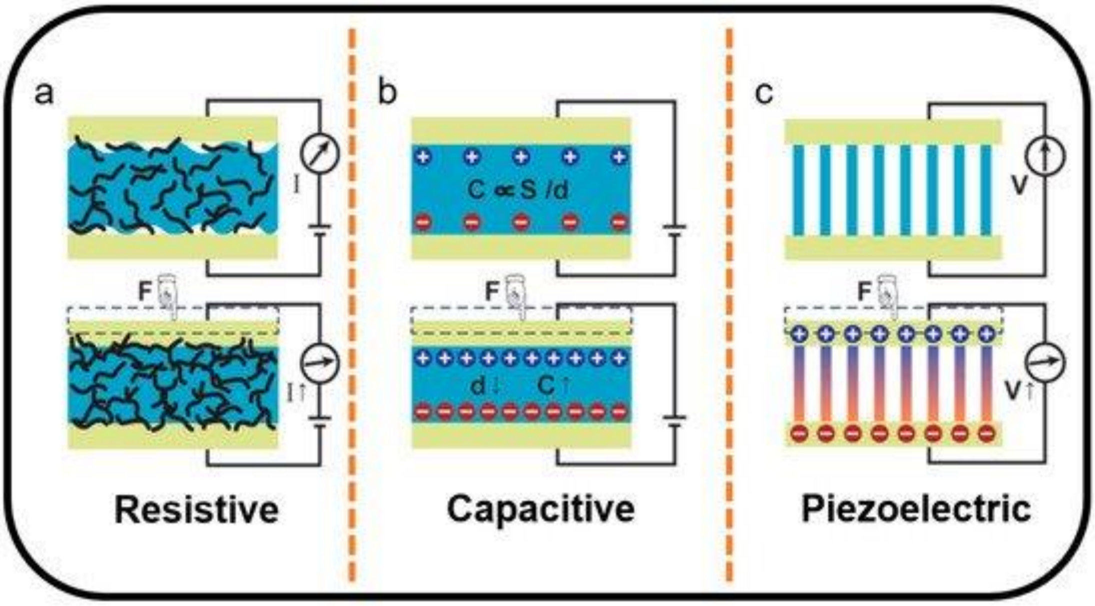

Figure 20- In this figure, ıt shows the mechanism of (a) resistive, (b) capacitive, and (c) piezoelectric sensors. Copyright 2015, American Association for the Advancement of Science (Zewei et al., 2019).

4.1 Resistive sensor

Resistive sensor commonly used in human motion detection and artificial intelligence applications. Resistive transducing based sensor converts external force to different resistance. In resistive sensor, by applying an external force on transducing sensor area, it is possible to change the resistive effect. Then it can be probed in terms of change in the electrical signals on resistive sensor surface. Resistive sensors are widely used because of its simple measurement method and large applications area. Since, resistive sensor can be fabricated by interfacing sensing material that are suitable to change external force to a conductive path, therefore graphene is a most suitable 2D sensing nanostructure to exhibit resistive effect in order to develop flexible strain and pressure sensors. Graphene based resistive sensors have many advantages such as detection range, simple equipment construction and signal testing.

4.2 Capacitive sensor

Another type of stain pressure sensor is a capacitive sensor which converts mechanical stimulus signals to displacement signals by detecting the force. Displacement signals cause a change in capacitance. This sensor can detect force in different variations by changing the area of sensing material and open space to parallel plates to obtain the electrical signal. Graphene nanostructure can be easily interfaced on flexible polymeric substrate that have compression properties of a dielectric layer, therefore graphene based flexible capacitive sensor showed excellent sensitivity and stability. Further, capacitive sensor can probe tiny force low magnitude signal and therefore recently showed tremendous development in the development of wearable electronic devices for human health monitoring applications (Nag, Mitra, & Mukhopadhyay, 2018).

4.3 Piezoelectric sensor

Pressure sensors are fabricated based on piezoelectric transduction mechanism and it is based on a transducer that converts pressure to measureable electrical signals. In this type of sensor, piezoelectric material used because it has non-centrosymmetric crystal structure which possess a dipole moment. Therefore, to design a sensitive pressure sensor the piezoelectric materials consider to have high piezoelectric coefficient. Graphene is emerged as suitable sensing materials because it can generate electrical charge under mechanical stress due to the graphene properties. Single-layer graphene has a negative piezoelectric conductance effect, but two-layer graphene has a positive piezoelectric conductance effect. Therefore, graphene and its derivative can be used to detect continuous static pressure signals and perpendicular vibrations due to their ultrafast response time and ultrahigh sensitivity (Zewei et al., 2019).

4.4 Parameters of strain and pressure sensor

There are several parameters to define the performance of strain and pressure sensors. The efficiency of strain sensor is defined by measuring the gauge factor parameter. The gauge factor is also called strain factor. This is a ratio of a relevant change in electrical resistance R to mechanical strain as described in equation (1) (Nag et al., 2018).

$$\textit{Gauge factor} \quad GF = | \Delta R/R_0 / \varepsilon | \quad (1)$$

Where ΔR represents the change in resistance and R_0 represent initial resistance and ε is the strain parameter.

There are several parameters that determine the performance of both strain and pressure sensors that include sensitivity, detection range, linearity, hysteresis, response time and relaxation time. For example, the sensitivity parameter for a pressure sensor is define by the ratio between the fractional changes in resistance divided by force as shown in equation (2).

$$\textit{Sensitivity} = | \Delta R/R_0 / \Delta F | \quad (2)$$

Where, ΔR represents the change in resistance and R_0 represent initial resistance and ΔF is the change in applied force.

The equation (2) can also be used to define sensitivity parameter for capacitive and piezoelectric pressure sensors (Zewei et al., 2019). Another important characteristic is sensor linear response and it is defined as linearity ratio of maximum deviation between the sensor calibration curve to the fitted line. Further, relaxation time and response time measure the speed of the response of the sensor at the loading and unloading process (Zewei et al., 2019). These are important parameters that determines the frequency of signal sampling identifies the materials used in the sensing layer of the sensors. Table 4 shows the graphene-based strain sensor performance as function of gauge factor parameter with respective to maximum attainable stain and linear response reported in the literature.

Cycling stability is an important parameter to enhance the performance of a strain sensor under a dynamic load. In particular, the stability of cycling is a key parameter to assess the efficiency of a strain sensor under a dynamic load. As shown in the (Fig.21), the poor cycling performance is unprocessed graphene versus graphene oxide combined with polydopamine and Ni^{2+}, which shows excellent sensing stability. These are important for fabricating wearable strain and pressure sensor applications. Graphene based sensors stain sensor promising due to cycling stability features and it proved that reversibility remained after even thousands of stretching cycles (Qi et al., 2020).

Table 4: Gauge factor as function of maximum attainable stain and linear response for graphene based stain sensor (Zewei et al., 2019).

Electrode material	**Gauge Factor**	**Maximum attainable strain (%)**	**Linearity in the response**
Graphene	~10^6	120	Non-linear up to 1%
	10^3	106.2	Linear up to 6%
	29	70	Linear up to77%
	300	<30 (Tunable GF)	Linear
	15-29	70	Linear
	7.1	100	Linear

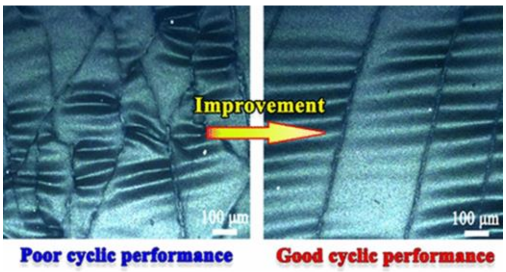

Figure 21- Poor cyclic is unprocessed graphene and good cyclic performance of reduced graphene oxide shows decrease in the deformation of the matter under strain (Qi et al., 2020).

4.5 Application of graphene based flexible strain and pressure sensor

4.5.1 Graphene based resistive flexible pressure Sensor

Flexible graphene pressure sensors have showed potential for developing soft and flexible electronic skin based wearable devices that can monitoring the human health/motion and can also be applied a variety of biomedical applications.

A flexible resistive-type strain sensor was developed through combining reduced graphene oxide (RGO) with thermoplastic polyurethane (TPU) by Want et al. (Yalong Wang et al., 2018). They synthesized RGO/TPU composite for flexible strain sensor using electrospinning and subsequent ultrasonication treatment. In electrospinning TPU pellets were dissolved in a mixed solvent (DMF:THF=1:1)(Yalong Wang et al., 2018). After TPU electrospun mats were immersed into well dispersed RGO solution with 20 min ultrasonic treatment and synthesis procedure and synthesized strains sensor are illustrated in (Fig.22)(A). RGO/TPU sensor demonstrated excellent stretchability and high sensitivity. Also this sensor shown good durability, stability and fast response. After 6000 cycles stretch and release it still cover his position. RGO/TPU resistive sensor can be attach to skin or clothes to monitor human motions and find many s applications in smart wearable devices.

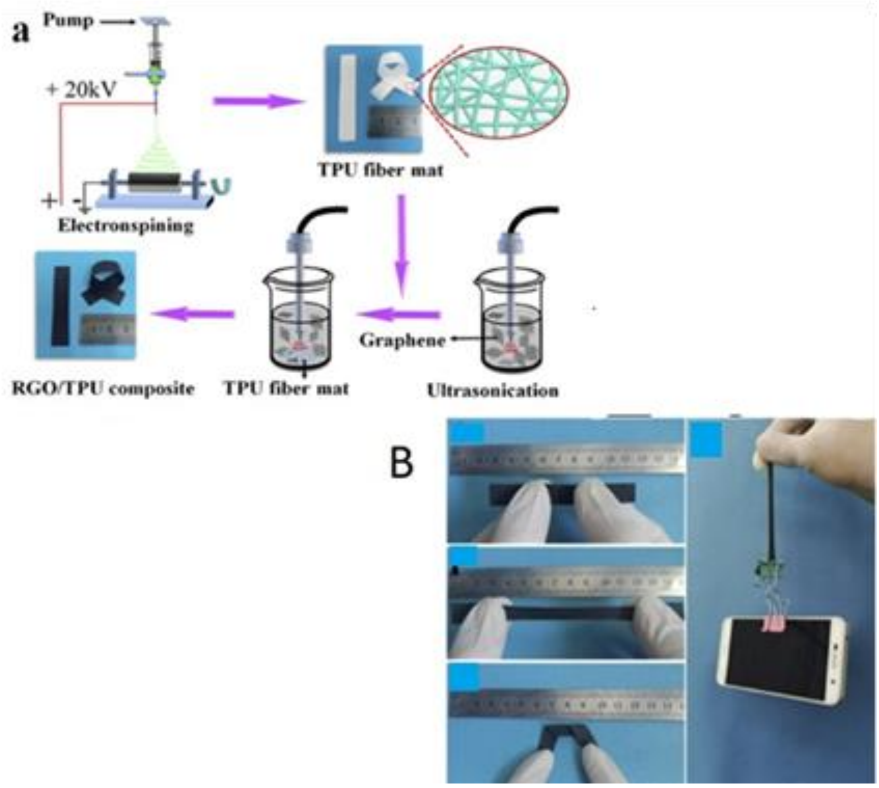

Figure 22- (A) it shows the fabrication process of RGO/TPU with steps and (B) it shows the stretchability of RGO/TPU strain sensor.

Tian et al. (Tian et al., 2015) fabricated laser-scribed graphene oxide film based resistive pressure sensor with a sensitivity of 0.96 kPa^{-1} in the range from 0 to 50 kPa.

4.5.2 Graphene based flexible piezo-electric sensor

Piezonic effect is very important parameter in nanomaterial in order to fabricate flexible electronic devices. Recently, Liu et al. fabricated solid polymer electrolyte (SPE)-coated graphene field-effect transistor(S-GEFT) piezoionic-powered strain and touch sensors (Liu et al., 2021). S-GFET fabricated using poly (ethylene 2,6 – naphthalate) (PEN) substrate and CVD graphene transferred with standard-wet transfer approach was used. Then electrode pattern by deposition of Cr (5 nm) and Au (50 nm). The SPE dropped casted on the graphene channel sensor electrode surface and fabricated S-GEFT showed in (Fig.23)I. S-GEFT was designed for touch sensing by coupling of triboelectrification to induce electronic transport in the S-GFET. The operation of this sensor was based on piezonic effect where the pressure applied to the sensor tuned the piezoionic doping to different dirac point voltage of sensor and piezoionic mechanism is schematically described in (Fig.23) A-B. While the sensor (S-GFET) operated as strain sensor through distinguishing the strain between compression and tension. The fabricated strain sensor was simple, sensitive and exhibited high gauge factor nearly 30 with a good stability.

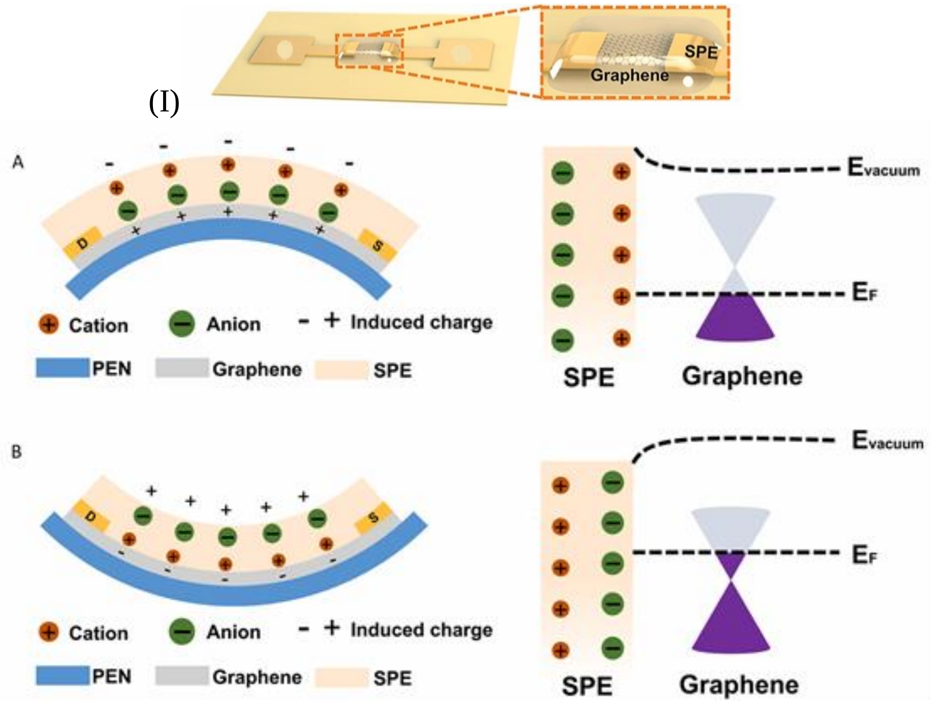

Figure 23- (I) SPE-coated graphene field-effect transistor. (II) In the left side it shows the ionic distribution and carrier doping state in the graphene channel. On the right side it shows the energy band diagram (A) tensile strain and (B) compressive strain (Liu et al., 2021).

4.5.3 Graphene based capacitive sensor

Flexible and stretchable graphene capacitive sensor based technology is important in the advancement of various wearable electronics. Graphene offers numerous benefits to fabricate flexible capacitive sensor such as mechanical flexibility and optical transmittance. Ismail et al. reported fabrication of flexible and sensitive graphene based strain sensor by coating graphene on polypropylene (PP) film (Ismail, 2019). The fabrication of graphene based sensor was fabricated by vacuum filtration method. Initially, oil control film was hydrophobic (PP), then pre-treatment of PP surface by THF allowed the adhesion of graphene coating on the film as shown in (Fig.24). The copper tape acts as an electrode while the Kapton tape was used to attach the fabricated sensor on the targeted body part. The fabricated flexible graphene-polymer based strain sensor using this approach demonstrated high gauge factor (~1000). The fabricated strain sensor could be used to monitor various subtle human motions such as wrist pulse finger bending and phonation recognition.

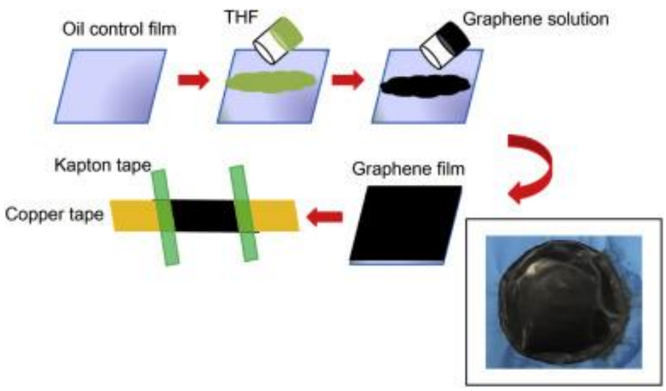

Figure 24- Schematic preparation of graphene-based strain sensor on oil control PP film by filtration (Ismail, 2019).

Recently, Yang et al. demonstrated fabrication of a novel three-dimensional microconformal graphene electrode for ultrasensitive and tunable flexible capacitive pressure sensors (Yang et al., 2019). They fabricated different structured flexible graphene electrodes that include smooth (SGrEs), nanostructured (NGrEs), and microstructure (MGrE). These were fabricated via traditional PMMA-mediated transfer method, UVA-mediated transfer method, and microconformal transfer method, respectively and shown in (Fig.26) (a-d). The sandwiched pressure sensor uses a microstructure graphene electrode as the bottom electrode, flat PDMS dielectric layer, and smooth graphene on the PET substrate as the top electrode (Fig.6e). The variation rate of capacitance depends on the relative dielectric parameters of multilayered materials and the electrode distance and can transduce the signal pressure signal in terms of change in capacitance as shown in Fig.6f-g. This approach showed high-performance capacitive pressure sensor with high sensitivity (3.19 kPa^{-1}), fast response (30 ms), ultralow detection limit (1 mg), tunable-sensitivity, high flexibility, and high stability. It is evident that the microstructure graphene electrode can effectively improve the sensitivity of capacitive pressure sensors and the sensitivity can be tunable with the controllable microconformal structure. The developed pressure sensors also demonstrated insect crawling detection, wearable health monitoring, and force feedback of robot tactile sensing with a sensor array.

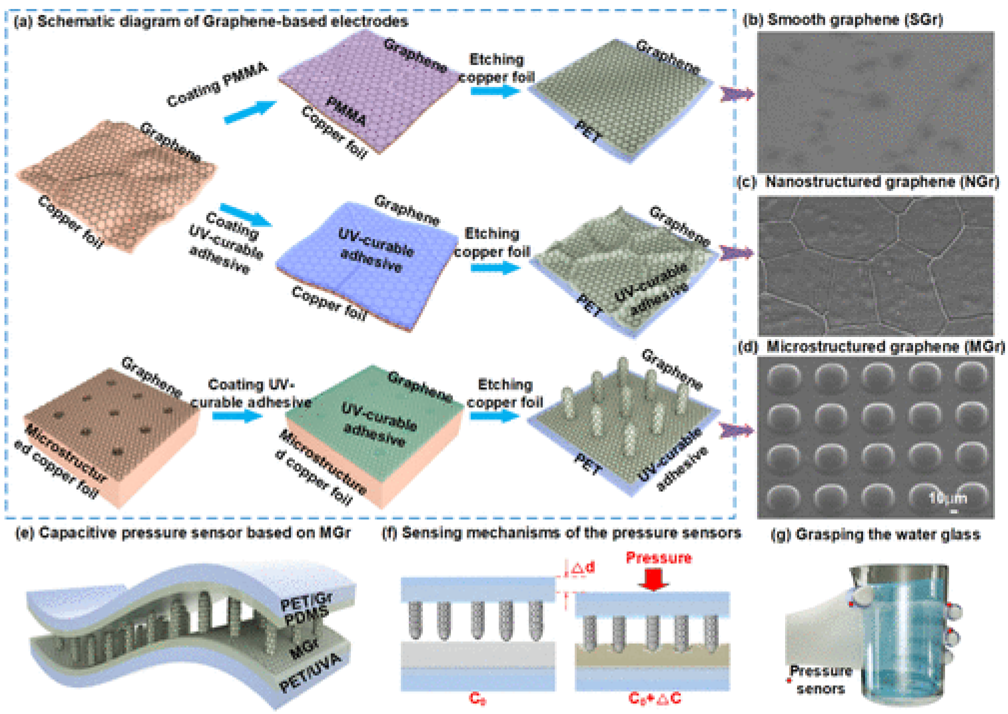

Figure 25- Fabrication of the flexible pressure sensors based on microconformal graphene electrodes. (a) Schematic diagram of fabrication process for different conformal graphene electrodes. (b–d) SEM images of SGrE, NGrE, and MGrE derived from PMMA-based, UVA-based and microconformal transfer methods, respectively. (e) Illustration of capacitive pressure sensor based on MGrE. (f) Schematic diagram of sensing mechanisms. (g) Schematic diagram of grasping with the proposed pressure sensor (Yang et al., 2019).

5.1 Wearable graphene-based glucose sensors

The use of sensitive wearable flexible glucose sensors in glucose detection of high blood glucose levels due to insufficient insulin production in diabetic patients is an innovative and functional method that has attracted considerable attention in recent years. Although current enzyme-based electrochemical glucose sensors are applicable with their sensitivity and selectivity; studies on glucose sensors that do not contain enzymes continue, as enzyme- based applications are sensitive to temperature, humidity, pH and chemicals due to the natural instability of enzyme molecules.

Porous laser-induced graphene (LIG) is an interesting and functional sensing carbon material because of its suitable for interfacing biological receptor/molecules for biosensing applications. Recently, Pt nanoparticles were decorated on porous graphene nano-layers were used as electrochemical sweat sensing electrode for the detection of glucose. For this first, LIG nanostructure was synthesized by significantly breaking the bonds in the polyimide by laser radiation with a heptagon and hexagonal lattice structure containing more than 85% carbon content (Yoon et al., 2020). Further, this study utilized acetic acid treatment of LOG to improve electrical properties of LIG. It has been reported that the increase in carbon-carbon bonds, which decreases the layer resistance, increases the electrical conductivity performance due to the high load transfer resistance (Fig.26). The surface modification of LIG treated with acetic acid was carried out by using facile dip-coating technique (Yoon et al., 2020).

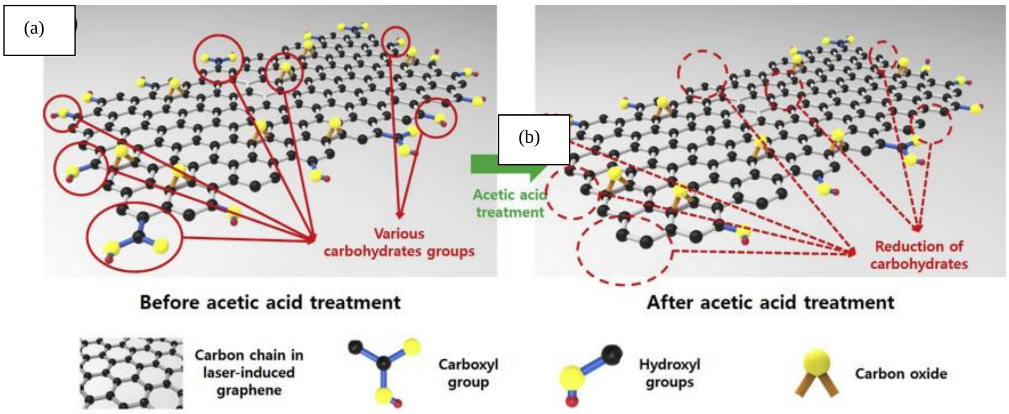

Figure 26- Comparative representation of the bond structures of the LIG electrode in the untreated (a) and acetic acid treated (b) states (Yoon et al., 2020).

As seen in Fig. 26, the ratio of carbon-carbon bonds has increased in graphene with the acetic acid treatment due to the decrease of carbonhydrate functional groups. Secondly, due to increase in the ratio of carbon-carbon bonds, clustering of nanoparticles during electrodeposition was prevented and a stable and homogeneous distribution of Pt NPs (nanoparticles) was achieved (Yoon et al., 2020). After the stable electrodeposition of PtNP with homogeneous distribution on the LIG, the immobilization of the chitosan-glucose oxidase (GOx) composite on the LIG/PtNPs electrode was achieved to fabricate the sweat glucose biosensor (Yoon et al., 2020). As seen in Fig. 27, The new enzyme glucose sensor produced with acetic acid treated LIG has a maximum 300 µM of the ultra-low detection limit (LOD) and sensitivity at least 4.622 µA/mMhe was observed (Yoon et al., 2020).

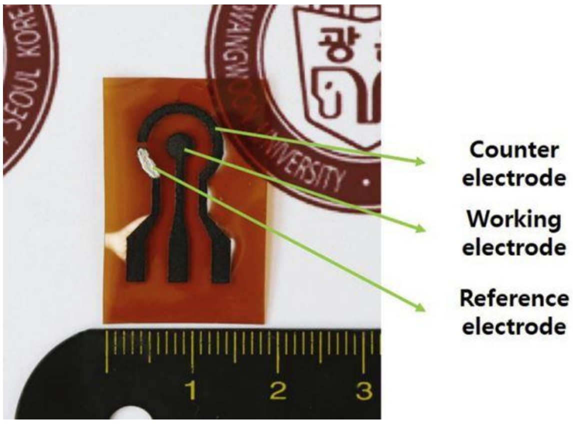

Figure 27- Fabricated enzyme glucose sensor LIG electrode on PI film (Yoon et al., 2020)

Recently, Cu-based nanomaterials are preferred for glucose determination compared to other metal-based ones due to their high electrocatalytic activity and stability, and it has been reported that their sensitivity in glucose determination will increase when combined with graphene (Y. Zhang et al., 2020). Zhang, Yue et al. developed an enzyme-free flexible glucose amperometric bio-sensor decorated with Cu nanoparticles fixed to a laser-induced graphene (LIG) composite using the substrate-assisted electroless deposition (SAED) technique (Y. Zhang et al., 2020). Choosing SAED, which is a new approach as the deposition process in reducing Cu metal to NPs, is convenient due to its redox potential, and it is also cheap and effective. As a flexible substrate, polymer polyimide (PI) film was chosen as a suitable choice with its mechanical, chemical and thermal resistance. LIG, besides its simple production, is a very suitable choice for electrochemical reactions with wrinkles and tears on the graphene surface (Y. Zhang et al., 2020).

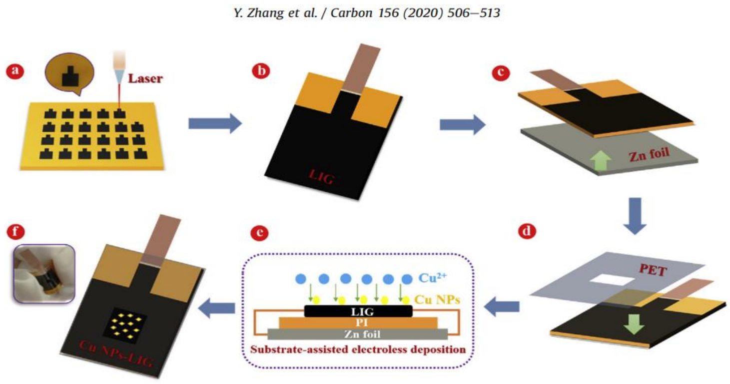

Figure 28- An Illustration of fabrication steps of the flexible Cu NPs-LIG sensor from (Y. Zhang et al., 2020).

In the simple manufacturing technique reported to be developed for flexible Cu NPs-LIG composite electrode to be used for glucose determination; first of all, black graphite is formed by carbonization and graphitization that occurs after PI film depolymerizes when exposed to intense laser radiation. Carbon monoxide and carbon dioxide are formed from graphitic carbon and O_2 and H_2O molecules, which reacts in high temperature and as a result of the applications 3 dimensional (3D) porous graphene was formed (Y. Zhang et al., 2020). As schematized in (Fig.28), in the firstplace etching of LIG with its pre-designed pattern on the flexible PI film was performed by means of laser radiation and this leads to formations of black carbonized layered LIG film and non-laser radiation PI film. These treated PI films are then cut into small pieces, densely containing LIG and then Zinc (Zn) foil of equal size as a substrate to SAED is bonded to the LIG layer in the PI film with silver paste. The LIG layer encapsulated with PI tape and polyethylene terephthalate (PET) was utilized to generate electrochemical signal detection by opening a 1 mm^2 section. The capsule LIG is placed in 0.01 M $CuSO_4$ solution and SAED process is started. As a result, Cu ions are reduced to Cu NPs. Finally, the zinc substrate and silver paste are removed and the Cu NPs- LIG sensor obtained is allowed to dry (Y. Zhang et al., 2020). Due to the excellent electrochemical properties of the Cu NPs-LIG, it has been used as electrochemical biosensor for the detection of glucose with high sensitivity of 495 mAmM 1cm^2, fast response time (less than 0.5 s) and LOD of 0.39 mM was achieved. The fabricated flexible bio-sensor was one of the examples among non-enzymatic wearable glucose diagnostic devices (Y. Zhang et al., 2020).

In the study by Yuan, Y. et al., the glucose bio-sensor was fabricated by immobilizing glucose oxidase (GOD) and 6-ferrocenyl hexantiol (Fc) with gold nanoparticles decorated with GOD/Fc/ Au/ SSLG, consisting of a graphene modified single layer on glassy carbon electroctode (GCE) (Yuan, Wang, Wang, & Hou, 2019). Gold NPs with a single layer of graphene support have low background current providing positive results in terms of electrochemical performance. In terms of immobilization of glucose oxidase and 6-hexanthiol, the large surface of the gold nanoparticle has been stated to be quite favorable (Yuan et al., 2019). Ferrocene derivatives have been used as electron vehicles to improve electron transfer. This study demonstrated wide glucose detection range (0.1 nM-5mM) with stability of sweat monitoring and has great potential for wearable bio-sensors (Yuan et al., 2019).

In another study by Peng, Y. et al., based on the fact that fiber-shaped microelectrode sensors are more advantageous in electrochemical detection of glucose compared to conventional electrodes (Peng, Lin, Gooding, Xue, & Dai, 2018). For this, a graphene fiber (GF) decorated with gold nanosheets (GD/AuNSs) with gold nanosheets was prepared by electrochemical deposition instead of conventional conductive fibers with low surface area (Peng et al., 2018). Gold nanomaterials exhibit high catalytic activity and low toxicity in the real-time biological monitoring field. The large surface area and high electrical conductivity of graphene fiber are utilized to support gold nanomaterials in the GF/Au hybrid, as the decoration of gold nanomaterials along the conductive fiber shaped electrode was utilized in wearable sensors. It has been stated that GF/AuNS sensor developed is suitable for the electrochemical detection of H_2O_2 and glucose with detection limits (1.62 and 1.15 µM) and sensitivity (378.1 and 1045.9 mM 1cm^2)(Peng et al., 2018).

5.2 Graphene-based wearable pH sensors

Accurate measurement of pH level in sweat is a helpful resource in determining many diseases such as diabetes, atopic dermatitis, fungal infections and kidney stones (Zahed et al., 2020). Flexible biosensors that can be integrated into human skin are interesting for their measurement based on continuous monitoring of such markers. It has been stated that most of the flexible electrochemical bio-sensors developed for monitoring biomolecules in sweat prevent mass production due to their complex production processes (Zahed et al., 2020). While this is the case, laser induced graphene (LIG), which stands out with its simple production process, has the possibility of loss of electrical performance as a result of deformation in graphene flakes due to its weak strength (Zahed et al., 2020). On the other hand, it has been stated that poly (3,4-ethylene dioxythiophene) -poly(styrene sulfonate) (PEDOT:PSS) provides electrical strengthening by acting as a binder in the pores of the LIG (Zahed et al., 2020). Zahed et al. fabricated LIG based flexible biosensor to detect human sweat pH. They developed cost effective and functional production method by utilizing the spray coating of PEDOT:PSS diluted with co-solvent on patterned LIG on PI substrate (Zahed et al., 2020) (Fig.29). In addition, due to the high pH-sensitive conductivity of polyaniline (PANI), PANI was used to modifying the working electrodes with electropolymerization of aniline. The fabricated sensor exhibited sensitivity in the pH range of 75.06 mV/pH (Zahed et al., 2020).

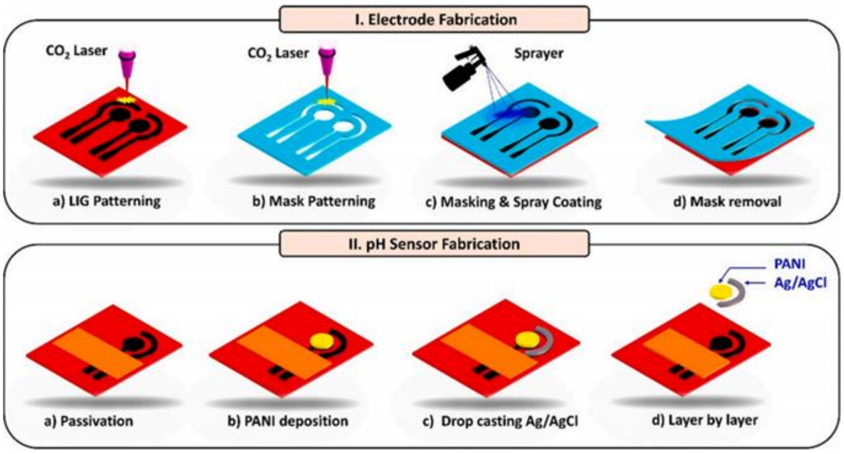

Figure 29- Production stages of biosensor are schematized with electrode and pH sensor production (Zahed et al., 2020).

The ability of wearable flexible biosensors to operate continuously without using an external battery is a milestone for health monitoring applications. Because, traditional Li-ion based (LiB) batteries are not suitable for wearable systems due to their negative aspects such as low performance, weight, bulkiness and heating problem (Manjakkal, Núñez, Dang, & Dahiya, 2018). On the other hand, supercapacitors are very promising for devices that require flexible and portable energy storage with their features such as fast charging times, high flexibility and no thermal degradation problem. To solve this problem, Manjakkal et al. fabricated a wearable CuO nanorod based chemically resistant pH sensors by integrating flexible self-charging power pack (FSPP) composed of a flexible photovoltaic cell (PV) into a porous graphene foam-based supercapacitor (GFSC) (Fig.30) (Manjakkal et al., 2018). The current density of the produced GFSC was observed as 0.67 $mAcm^2$, field capacitance (CA) 38 $mFcm^2$, energy density (EA) 3.4 $\mu Whcm^2$ and power density (PA) 0.27 $mWcm^2$ (Manjakkal et al., 2018). The self-powered flexible wearable bionsensor in this study showed the change in the response speed of pH sensor which is less than 5s with pH range 6.38 to 4.

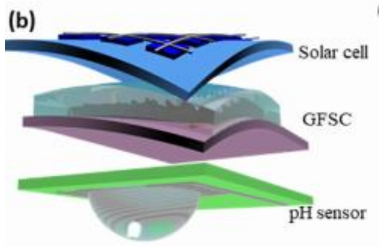

Figure 30- 3-D representation of FSPP created by photovoltaic cell (PV) and graphene foam-based supercapacitor (GFSC) which can produce a continuous DC power to the wearable Cuo nanorod based chemically resistant pH sensor (Manjakkal et al., 2018).

6. Conclusion and future perspective

Graphene and graphene-based derivatives have been used as new transducing sensing elements in developing flexible sensors for wearable electronics due to their unique optical, electrical, mechanical, and thermal properties. We have summarized the status of graphene based flexible gas, humidity, temperature, strain and biosensors focused on flexible transducer enabled fabrication strategies, materials and devices in combination with passive polymeric materials for flexible electronic skin sensors. Flexible graphene-based hybrid not only exhibit high sensitivity toward gases, temperature, biomolecules but also show promise for developing flexible, transparent, and stretchable strain sensors for wearable electronics. Graphene and its derivatives such as, GO, and rGO in combination with inorganic, and organic materials for applications in gas, stain and biosensors are also developing rapidly. As discussed above, graphene-based materials shown great potential to design and fabricate transparent and flexible sensors that could be used for wearable electronic devices. Nevertheless, there are still many aspects of graphene based flexible electronics that must be further developed that include sensor usability and noninvasive health monitoring and their large-scale manufacturing for multisensory applications. The recent advances in flexible gas, strain and biosensors sensors for wearable technology are at an early stage. There is continuous progress made on improvement of graphene-based flexible and wearable strain sensors for human health monitoring such as human body activities, which may allow to real commercial applications in the near future.

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