Semester: I/II						
CHEMISTRY OF SMART MATERIALS AND DEVICES (Category: Professional Core Course) Stream:CS (Theory and Practice)						
Course Code	**:**	22CHY12A		**CIE**	**:**	100+50 Marks
Credits: L:T:P	**:**	3:0:1		**SEE**	**:**	100 Marks
Total Hours	**:**	42L+ 30P		**SEE Duration**	**:**	3 Hours

Unit 4. Smart materials for sensors

"The students should be able to understand the importance of chemistry and nanomaterials for designing the smart devices and sensors for engineering and biomedical applications. For the design of smart devices (RFID) and sensors (electrochemical/piezo), the significance of electromagnetic property of materials, redox chemistry, and understanding the electrocatalytic nature of materials is discussed. Students can also realize the Radio Frequency (RF) IDs made of graphene, CNT based wireless applications. The importance of synthesizing and functionalizing the novel nanomaterials such as carbon nanotubes, graphene and polyaniline can be understood for developing smart devices".

Lecture plan: Smart sensors and devices

Lecture-1: Introduction to smart materials and technology, Internet of things, Internet of nanothings.

Lecture-2: RFID device, meaning, working principle of RFID, classification of RFID tags, (Based on the availability and frequency), Materials for RFID tag (CNT, Graphene, polyaniline)

Lecture-3: Carbon nanotubes (CNTs)-meaning, types, structures; Synthesis by CVD method, functionalization-physical, chemical; properties

Lecture-4: Graphene-meaning, structure of graphene; Synthesis by Modified hummer's method, functionalization-physical, chemical; properties

Lecture-5: Polyaniline-Synthesis via chemical oxidative polymerization of aniline, different structures of Polyaniline, electronic properties, Applications of CNT, Graphene in logistic information, intelligent packaging systems

Lecture-6: Sensors: Introduction, types of sensors (Piezoelectric and electrochemical)

Lecture-7: Strain sensors- working principle, nanomaterials used, applications

Lecture-8: Electrochemical Sensors- working principle, types of electrodes, significance of each electrode, sensing mechanism.

Lecture-9: Applications of Electrochemical sensor for biomolecules-Glucose-Diabetic management, Vitamin-C (Ascorbic acid) Electrochemical-VOCs, and Gas sensor

Internet of Things (IoT) and Radio Frequency Identification Technology (RFID)

Internet of Things (IoT) technology: It is s new technology being developed in 1999. The purpose of this technology is that to connect, communicate, control and operate the activities of all the things through internet. This technology in an integration of hardware (sensors, telecommunication) devices and software programs. This technology is an integration of internet and sensor network, via (Radio Frequency Identification) RFIDs devices. If this technology involve the smart devices made-up of nanomaterials, it is called Internet of nanothings (IONTs). It interconnects the nanoscale devices with the Internet and the present communication technology.

RFID: It is a wireless, an electronic device/tag, which uses electromagnetic field to identify, track and connect with the objects attached with tags. The required data/information of the object is collected and recorded by means of radio frequency signal. It is expected that this tag should be able to function autonomously without the involvement of human in any harsh environmental conditions.

Working principle of RFID system:

- The RFID system consists of RFID TAG, ANTENNA, TRANSPONDER, READER, COMPUTER
- RF signals with a specific frequency are transmitted by READER through ANTENNA.
- When 'RFID TAG' enters the 'READER' area, the ANTENNA will transmit induced current, which activates the 'RFID TAG' to transmits the information to the 'READER'. (Passive system)
- In case of active system, when the RFID TAG enters the READER area, the embedded battery powers the RFID TAG in order to complete the communications with each other.
- After 'READER' reads the self-coded information, it will send the same to 'COMPUTER' for exchanging and managing the data.

The schematic representation of RFID working principle is shown below:

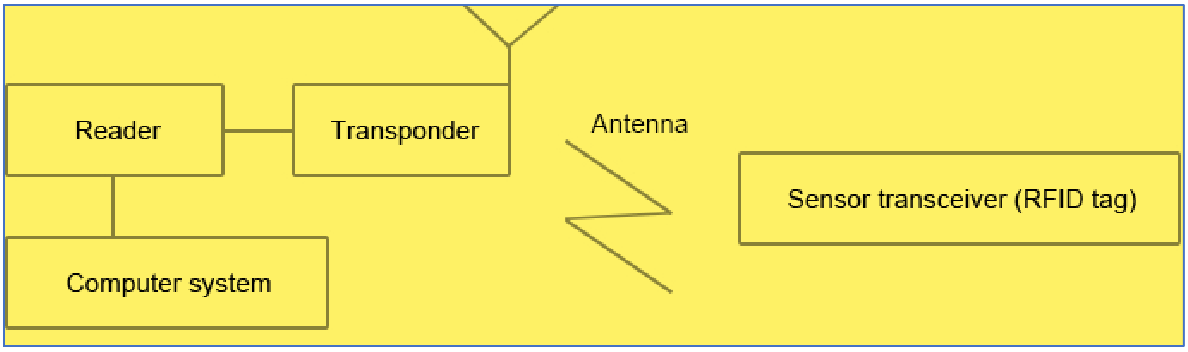


Figure 4.1. RFID working principle

Classification of RFID tags

Based on the power requirements, the RFID is classified as follows:

1) **Passive RFID Tag:** It is a RFID tag with no inbuilt power source (Battery) designed to use in small range (up to 10 m) tracking systems, operates on low, high or ultra-high frequency. However, it receives power from the reading antenna, whose electromagnetic wave induces a current in the RFID tag's antenna. It is very thin and has a long service life.
2) **Active RFID Tag:** It has its own power source, such as battery, inbuilt. It is used for long scanning and reading range (up to 100 m), operates only at high frequency. The price is relatively high, volume is larger than the Passive tag because of the built-in battery.

Further, the RFID is classified based on the working frequency range.

Types	Low-Frequency	High-Frequency	Ultra High-Frequency
Frequency Range	100~500 KHz	10~15 MHz	850~950 MHz~2.45 GHz
inductive distance	shorter	longer	longest
reading speed	slower	relatively high	fastest
penetration ability	good	Avearge	bad

Materials for RFID tag:

The RFID tags are fabricated by low cost inkjet-printed technique. Various types of conductive inks with different fillers such as metal nanoparticles, carbon nanotubes (CNT), graphene and polymer (polyaniline) have been developed for printed electronics. For the fabrication of RFID Tags, carbon nanotubes, graphene and polyanilines are generally used, as they can be used as inks for ink jet printing of RFID tags**.**

(For more understanding read: ***https://doi.org/10.1039/C7RA07191D****)*

Carbon Nanomaterials:

Carbon nanotubes are a new form of a hexagonal network of carbon atoms rolled up in the form of cylindrical shape.

Types of CNTs:

1. **Single-Wall Nanotube (SWNT) (Arm Chair, Zig-Zag and Chiral)**
2. **Multi-Walled Nanotubes (MWNT)**

- Multiple rolled layers of graphene sheets

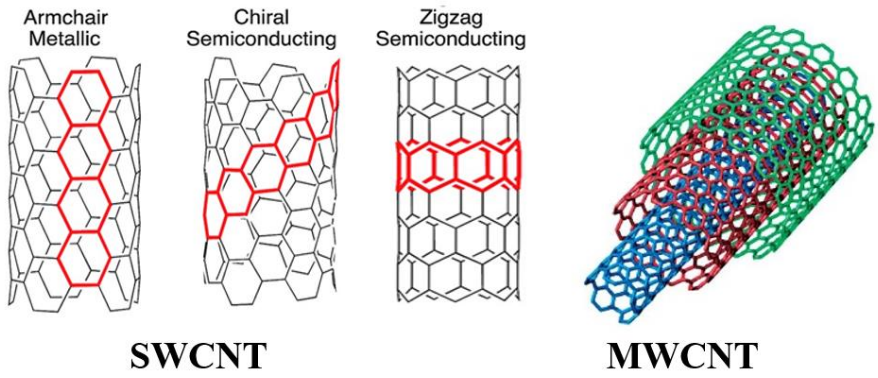


Figure 4.2. Types of carbon nanotubes

Synthesis of CNTs by modified CVD method:

Chemical Vapor Deposition: Requirements**:**

- High Temperature Tubular furnace (500 to 1500 °C)
- Source of Carbon: Methane, ethylene, hydrocarbon gas, xylene, natural gas
- Substrate: carbon, quartz, silicon
- Inert gas: Argon, Hydrogen, Nitrogen
- Catalyst: Ferrocene, Nickellocene, Cobaltocene

Principle: In this technique, carbon nano tubes grow from the decomposition of hydrocarbons at temperature range of 500 to 1200 °C in the inert atmosphere on the catalyst activated substrate.

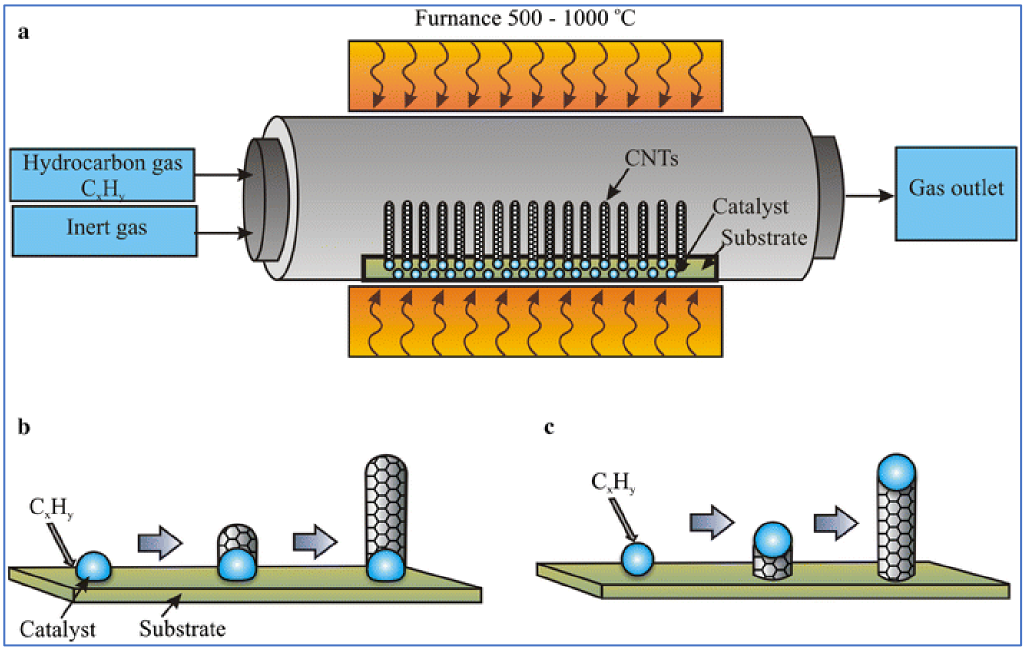


Figure 4.3. CVD experimental set up used for synthesizing carbon nanotubes

Ref: *Zaytseva et al. Chem. Biol. Technol. Agric.* ***3****, 17 (2016).*

https://doi.org/10.1186/s40538-016-0070-8

Furnace: The instrumental setup consists of a tubular furnace equipped with an inert atmosphere setup, temperature and reactant precursors flow controller.

Steps: Procedure involves as follows

- ❖ The cleaned quartz/carbon/silica substrate is placed in the middle of the tubular furnace.
- ❖ In order to maintain the inert atmosphere inside the furnace, initially the air/oxygen present inside the tubular furnace has to be removed by passing the argon or nitrogen gas for about 30 min.
- ❖ After maintain the inert gas atmosphere, the required temperature is set with slow heating rate.
- ❖ The hydrocarbon precursors in gaseous forms along with ferrocene and Benzene/toluene vapors are pumped into the reaction chamber.
- ❖ The furnace is heated up to 850–1000 °C and 550–700 °C for SWCNT and MWCNT production respectively.
- ❖ Initially, at high temperature, due the thermal decomposition of hydrocarbon, carbon atoms are formed are dissolved in the metal nanoparticle catalyst.
- ❖ Once the threshold concentration of carbon in the catalyst reached, a semi fullerene cap type of structure is formed due to precipitation of carbon atoms. This acts as a seed for further crystal growth, which further continues to grow in tubular form results in to CNT.
- ❖ After the formation of CNT on catalyst is completed as shown in the above figure, the supply of the reactant/catalyst varpors are stopped.
- ❖ Then the furnace temperature is reduced slowly to room temperature and supply of the inert gas also stopped.
- ❖ The CNT formed on catalyst is taken out along with the substrate, subjected to purification.

<u>Mechanism of CNTs growth:</u>

1. **Diffusion** of Hydrocarbon gas
2. **Adsorption** of Hydrocarbon gas on the surface active site of catalyst particles.
3. **Dissociation** (Homolytic fission) of Hydrocarbon in to highly reactive free radicals of ‘C’ and ‘H’.
4. Repetition of steps 1, 2 and 3 leading to increase in concentration (saturation) of free radicals.
5. **Precipitation** (aggregation) of carbon free radicals results into crystal growth in the form tube on the surface. ‘H’ free radicals escape as H_2 gas.

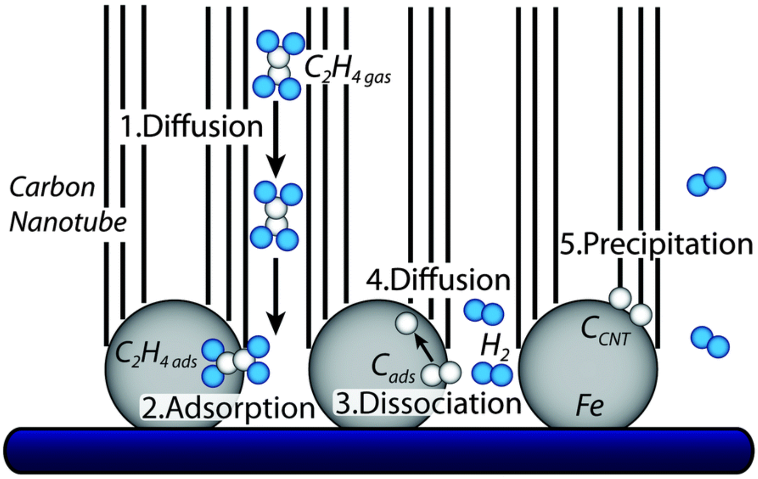


Figure 4.4. Steps involved in CNTs growth.

Functionalization of CNT:

CNTs are non-polar in nature and hence may not have chemical affinity/solubility in water or organic compounds. Therefore, the application of pure CNTs is limited. The modification/ functionalization of CNTs with functional groups like –OH, -COOH, $-NH_2$, $-NHCONH_2$ etc , makes it the most attractive and ultimate candidate for many biomedical and engineering applications. The modification/ functionalization of CNTs can be simply divided into

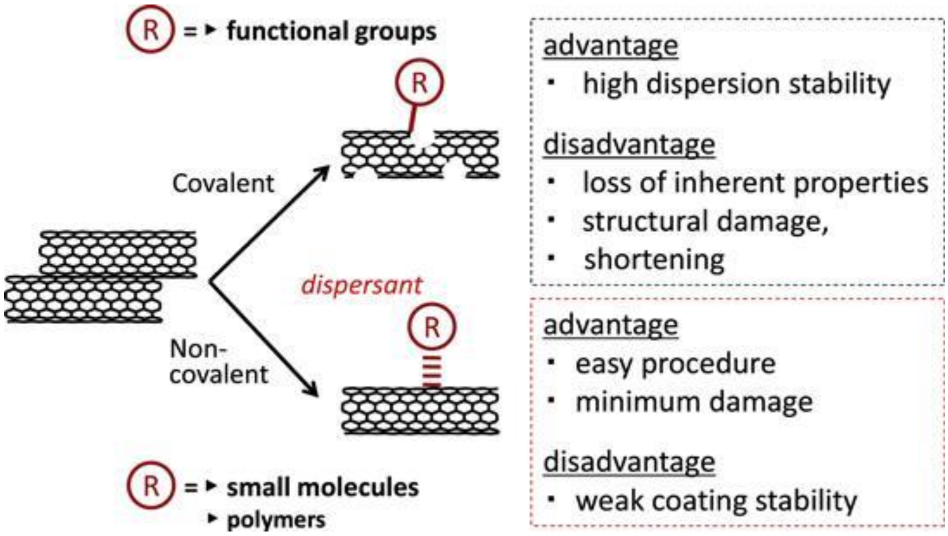
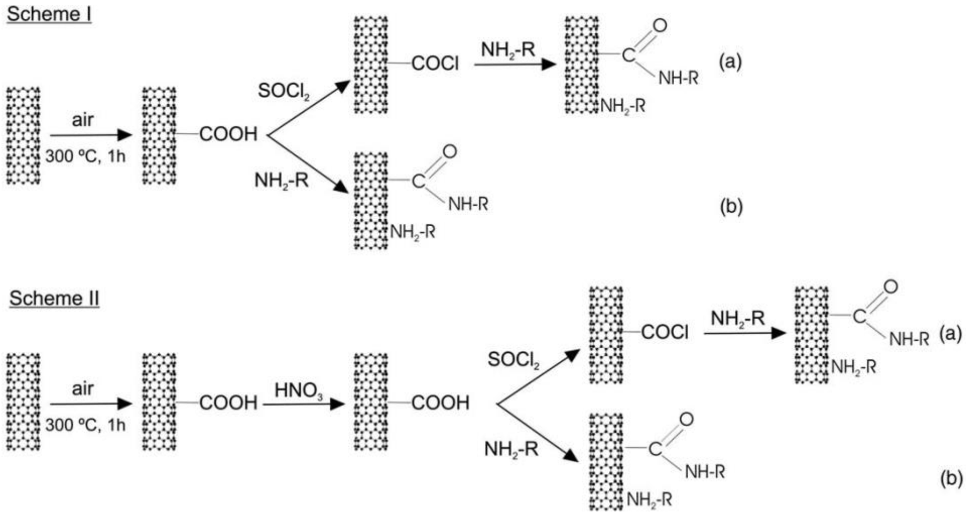


Figure 4.5. Types of CNTs functionalization.

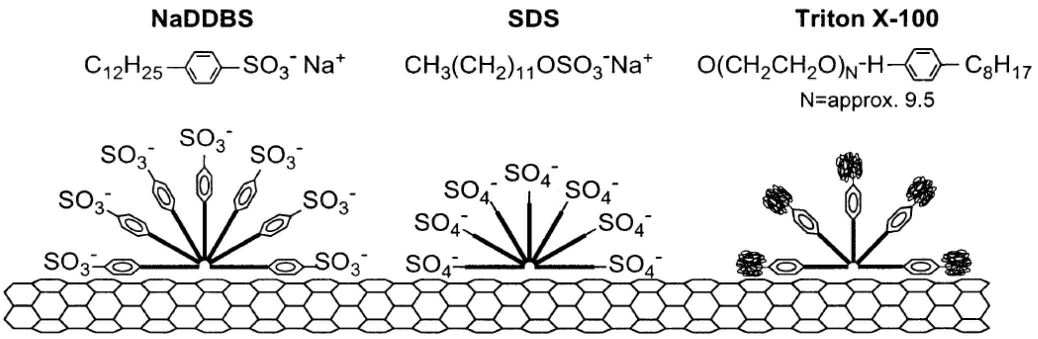
a) **Chemical (covalent) functionalization:** It involves the formation of true chemical bond between CNT and functional groups. The functional groups can be attached to the edge or side wall carbon atoms, which results into different properties. Direct covalent sidewall functionalization is associated with a change of hybridization from *sp2 to sp3 and a simultaneous loss of p-conjugation system.*

b) **Physical (Non-covalent) functionalization:** It involves the physical binding of molecules, metallic atoms, polymers with CNT by vander wall's forces**.** Like in case of covalent functionalization, it does not destroy the conjugated system of the CNTs sidewalls. Therefore the most of the structural properties of the CNT is still retained. The CNTs are functionalized non-covalently by **aromatic compounds**, **surfactants, and polymers,** employing ***π-π stacking or hydrophobic interactions***.

Examples for Chemical (covalent) functionalization:



Physical (Non-covalent) functionalization:



Applications of CNTs:

- RFIDs, Sensors, IoNTs sensors
- Optoelectronic devices (Field Emission Display (FED))
- As *electrodes in* batteries, *capacitors and super capacitor electrodes*.
- As *electrode catalyst supports in Polymer Electrolyte Membrane (PEM) fuel cells*
- *Hydrogen* Storage material in hydrogen fuel car.
- As electrically *powered artificial* muscles.
- Electro catalyst for water splitting, H_2 production.
- Adsorbent and photocatalyst for organic pollutants degradation.
- Sensor for heavy metal ion, gases, volatile organic compounds and biomolecules.
- Drug carriers

Graphene: Graphene is a newly found allotrope of carbon, consisting of single layer atoms in hexagon pattern. It is a purely carbon-based, honeycomb-structured, one-atom thick layer of carbon atoms (two dimensional sheet), bonded to one another by sp2 hybridization.

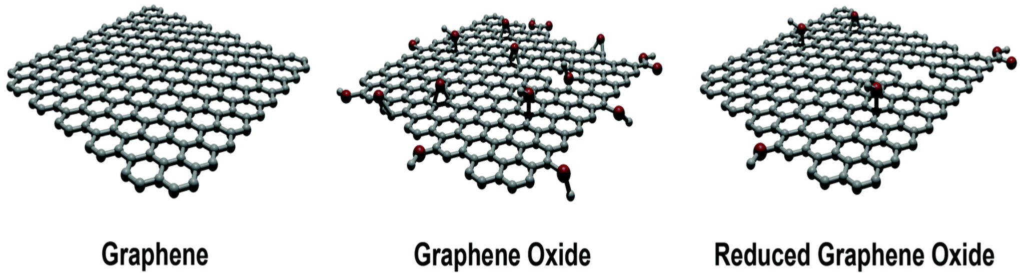


Figure 4.6. Structures of Graphene, Graphene Oxide and Reduced Graphene Oxide.

<u>Synthesis of Graphene Oxide and Reduced Graphene Oxide-Modified Hummer's Method:</u>

In a typical procedure, graphite (2 g) and $NaNO_3$ (2 g) were combined with H_2SO_4 (90 ml) in a 500 ml glass beaker and stirred for 30 min in an ice bath. Then $KMnO_4$ (10 g) is slowly added to the above solution under ultra sonication at 50°C for 2 h. About 200 ml of distilled water and 12 ml of H_2O_2 (35%) are then slowly added to the above solution, and the resulting solution is washed with dil HCl (10%) followed by concentrated HCl (37%). The washed product is dried in hot air oven at 80 °Cfor 24h. The final product obtained is called graphene oxide (GO) powder. The GO powder is further subjected to reduction by reacting with sodium borohydride. In addition to this, thermal, or photo-thermal reduction methods are also used to obtain reduced graphene oxide (rGO) structure.

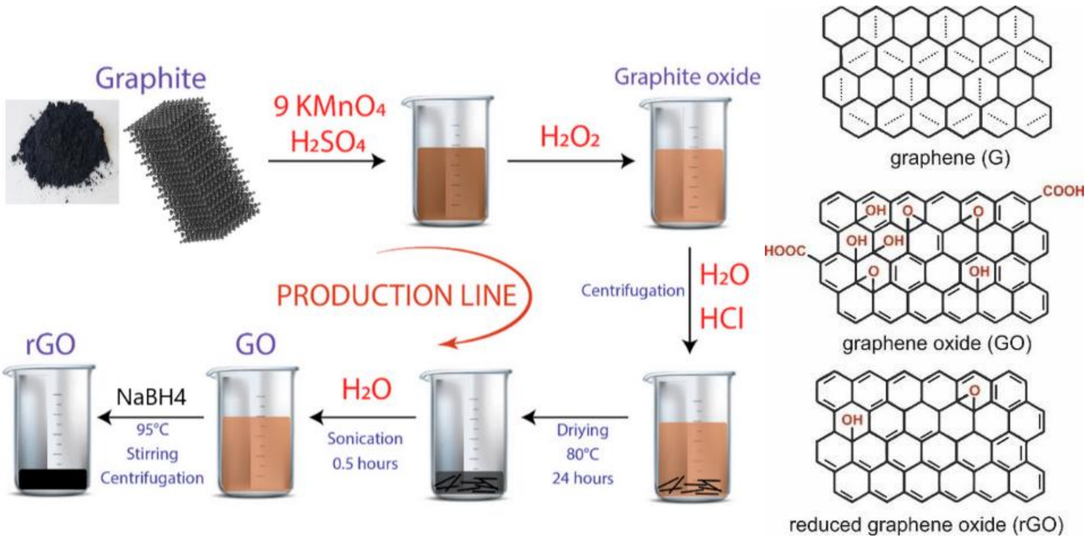
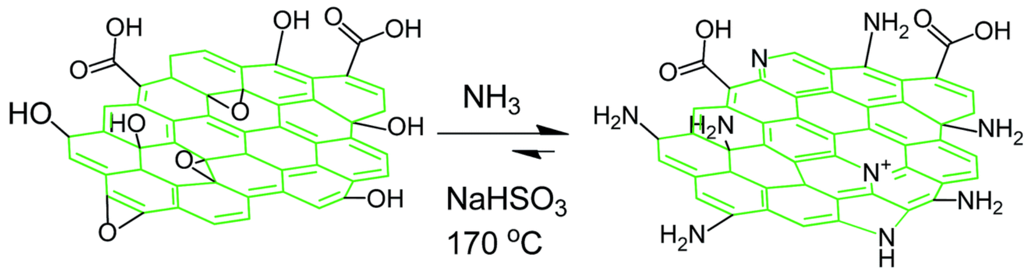


Figure 4.7. Modified hummers method steps for making graphene oxide

Functionalization of Graphene

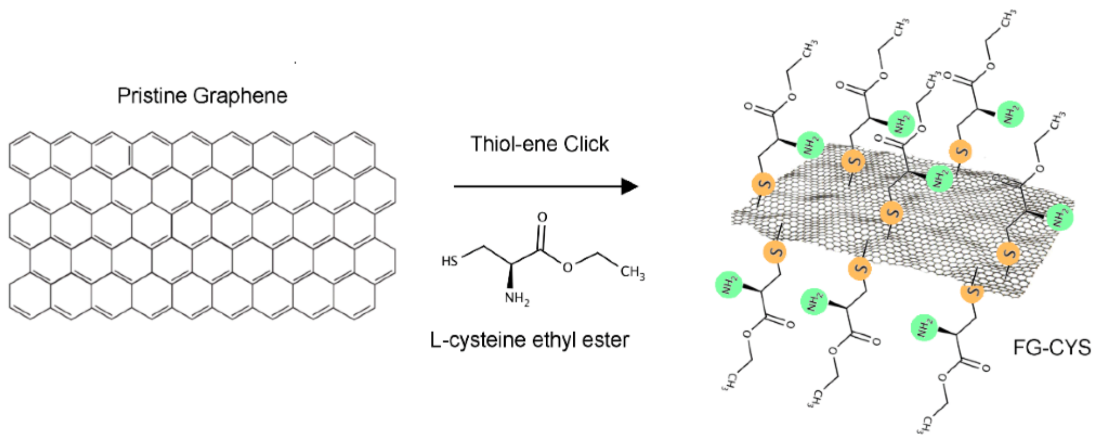
The functionalization is similar to CNT. It has two types (1) Covalent (chemical) and (2) Non-covalent (Physical) functionalization. The functionalization reduces the cohesive force between the graphene sheets and also to manipulate the physical and chemical properties.

The graphene oxide can be functionalized with amine group as follows.

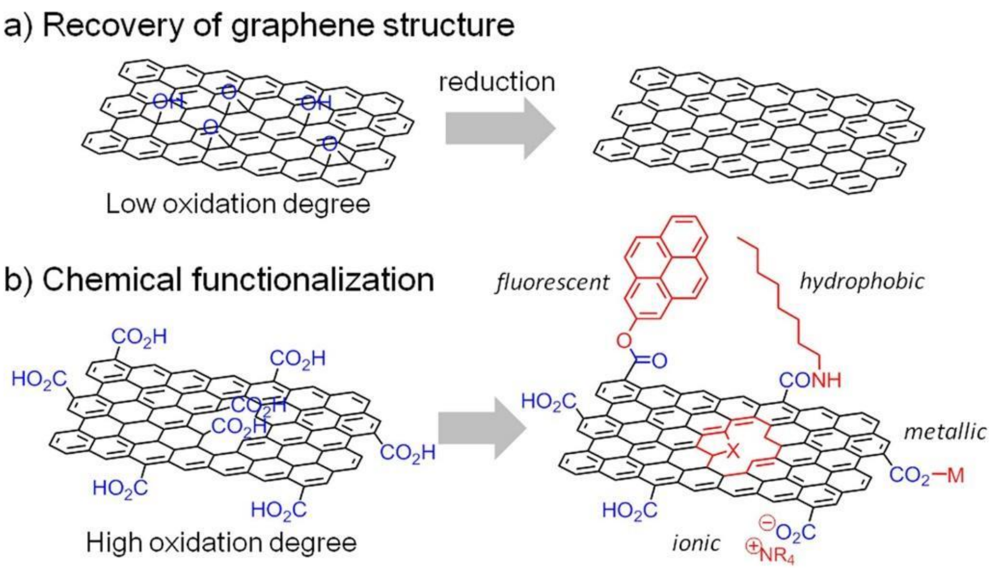


Ref: https://doi.org/10.1039/C5CC08252H

The graphene oxide can be functionalized with cysteine and thiolene group as follows.



Ref: https://doi.org/10.3390/ma14112830



Ref: https://doi.org/10.1038/srep21715

Graphene Applications

RFID, IoNTs, Solar Cells, Batteries, Fuel cells, Medicine (Drug Delivery, Cancer Treatment, Gene Delivery, Photothermal Therapy, Diabetes Monitoring, Dialysis, Bone and Teeth Implantation, Tissue Engineering and Cell Therapy), UV Sensors, Biosensors, Transistors, Wearable Electronics, Flexible Screens, Optoelectronics, Optical Sensors, Water Purification, Desalination, Lubricants.

Polyaniline

- ❖ Polyaniline (PANI) that has been extensively used as conducting polymer.
- ❖ Band gaps in the reduced and oxidized form of polyaniline are 4.3 and 2.7 eV respectively.
- ❖ Intrinsically conductive polymer used in various applications, including drug delivery, photovoltaic cells, plastic batteries, display devices, microelectronics, chemically modified electrodes, corrosion protection, and polymer light-emitting diode (PLED) displays

Preparation of Polyaniline

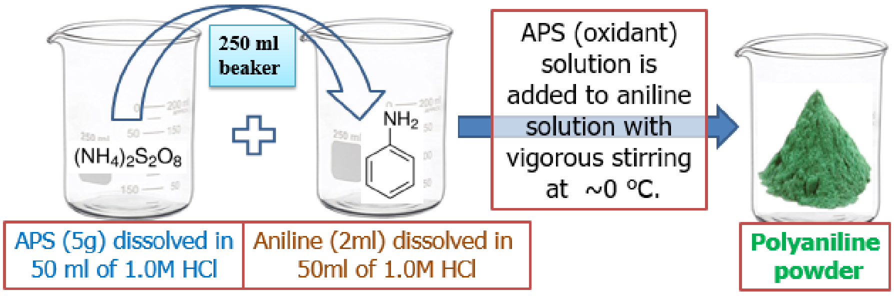


Figure 4.8. Reaction of polyaniline synthesis

- ❖ After the polymerization reaction, the resultant mixture is filtered and washed successively using 1.0M HCl followed by double distilled water, several times until the washings become colorless.
- ❖ Finally the residue was washed with acetone and dried at 60 °C.

The reaction mechanism of conversion of aniline to conducting polyaniline is as shown beloew.

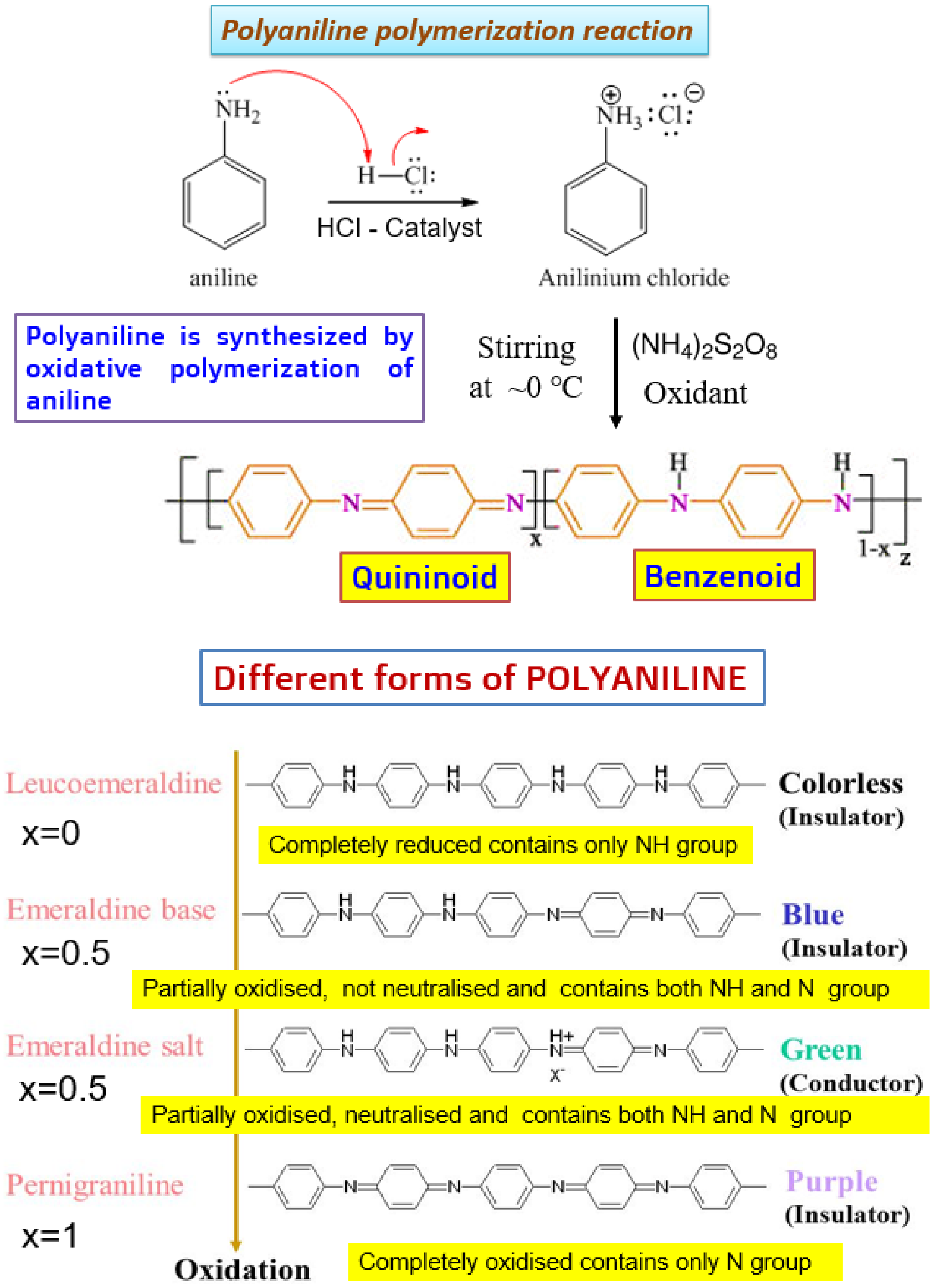


Figure 4.9. Structural differences of various forms of polyaniline –conducting and insulating forms

Sensor

It is device that measures change in a physical (heat, light, sound, pressure etc) and/or chemical (pH, smell, taste, concentration, humidity etc) parameters of interest in an environment and transforms it into an electronic signal.

Transducer: A transducer is a device that transforms a signal from one energy form to another energy form.

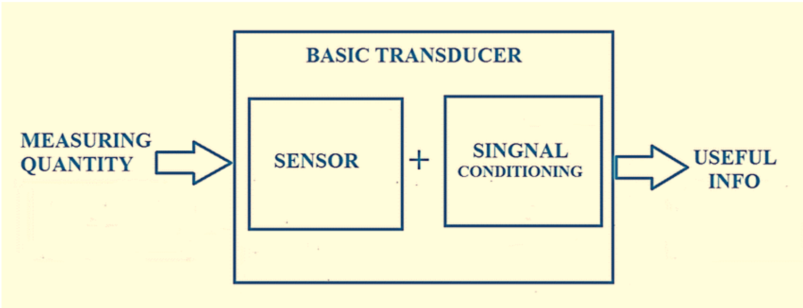


Figure 4.10. Schematic representation of sensor device

Piezoelectric (PE) Sensors

"Piezo" is word derived from Greek, it means for "press" or "squeeze". A piezoelectric sensor is a device, which converts physical parameters like acceleration, strain, pressure, vibration, temperature, or force into an electrical charge which can then be measured. The schematic representation of PE sensor is shown below.

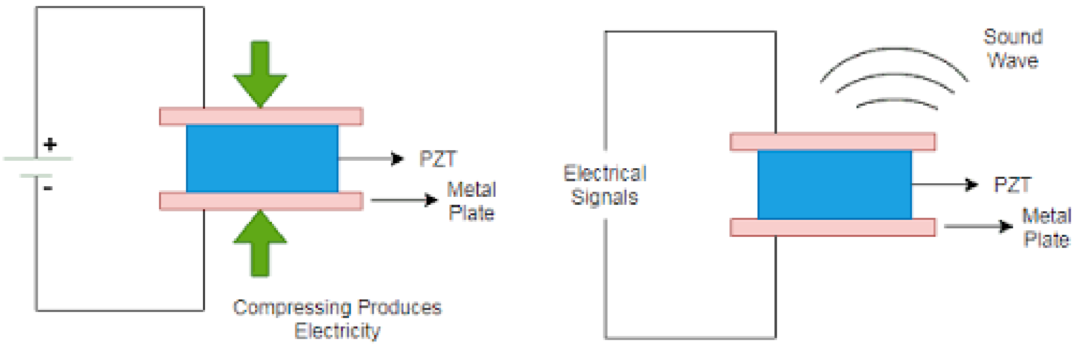


Figure 4.11. Schematic representation of Piezoelectric sensor

The PE sensor is widely used in biomedical, wearable electronics, and self-power energy harvesting devices. The piezoelectric sensors are mostly fabricated by using the perovskite ceramic material (lead zirconate titanate (PZT)) and also other lead-free ceramic piezoelectric sensors using bismuth sodium titanate (BST), barium titanate ($BaTiO_3$), boride and silicide ceramics (TiB_2, $TaSi_2$, WSi_2, etc.).

Characteristics of PE sensors:

The good PE sensor should exhibit:

High strength, High stability, High voltage output, Highly flexible, Wide frequency range, Impact resistance, High mechanical strength, Elastic compliance etc

Strain Sensor: Upon applying the external force on an object, the strain (permanent/temporary) is induced in the object due to its structural (internal) deformation, this results in change in internal resistance of the object, which can be measured by using the device called strain sensor. Various nanomaterials like graphene, CNT, PVDF, and their hybrids are used in these sensors.

Strain sensors widely used in flexible and wearable electronic devices for medical applications, civil engineering structures, mechanical engineering, aircrafts structures, etc

Strain sensors are widely used in medical industry applications, are as follows:

- **Pulse measurement** – PE sensors are very sensitive to record pulse measurements and effective in monitoring the patients' health.
- **Stethoscopes** – Due to high sensitivity and robustness PE sensors, they are often used within stethoscopes.
- **Anaesthesia Effectiveness** - PE sensors are capable of accurately measuring the muscles stimulations, and hence can be helpful in understanding the effectiveness of anaesthesia.
- **Sleep Studies** - PE sensors can be attached to various parts of the patient body and can be used to measure the smallest movements of patients during the sleep also.

PE sensors are very popularly finds their application in wearable and stretchable electronics used in healthcare and biomedical engineering, sport performance monitoring, soft robotics, and gaming and virtual reality.

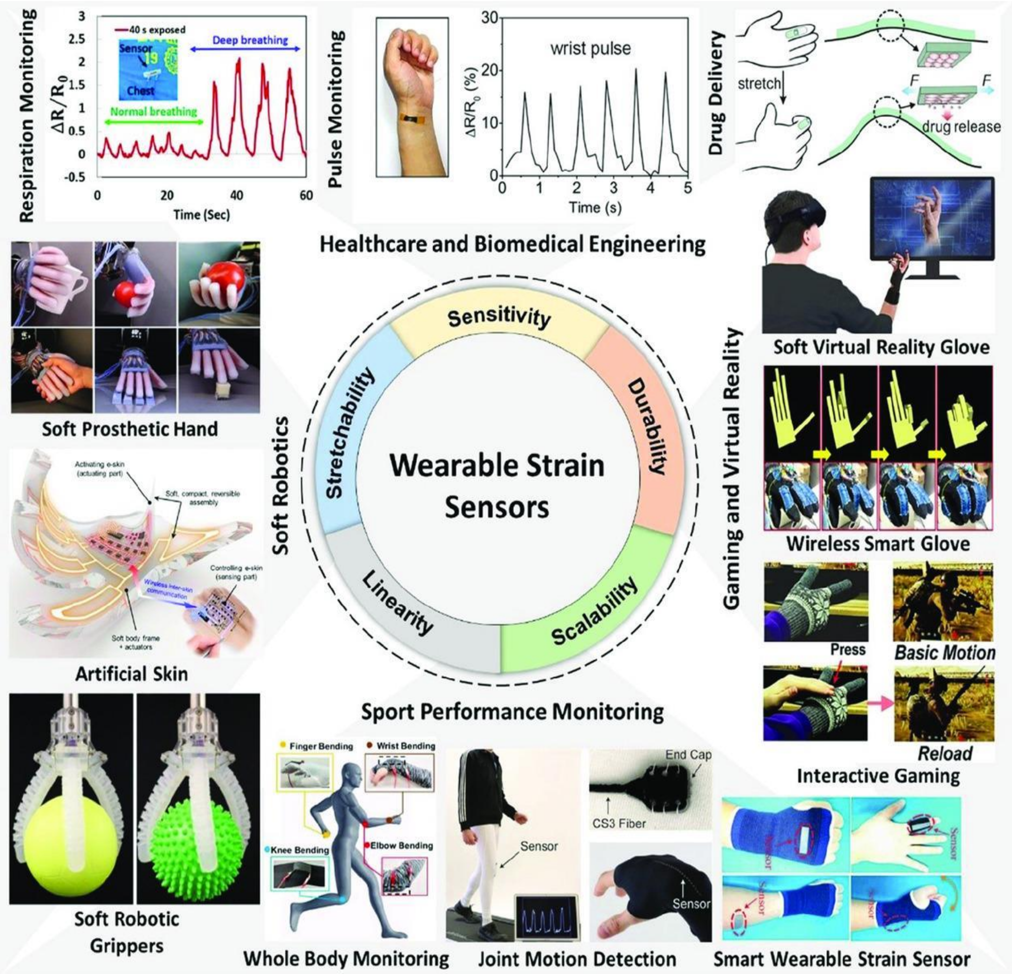


Figure 4.12. Wearable and stretchable strain sensors and their potential applications [for more understanding read: https://doi.org/10.1002/aisy.202000039]

Electrochemical (EC) Sensors: a device that converts chemical composition data of the analyte into an analytically usable signal.

Working principle: The basic principle of EC sensor is that it measures the current produced by chemical reactions in the electrochemical system. The main components of the sensor are (a) electrodes system, (b) transducer (c) amplifier and (d) recorder.

In electrochemical sensor, the electrode system consist of three electrodes such as working electrode, counter/auxiliary electrode and reference electrode. It has a potentiostat, which is an electronic instrument that controls the voltage between two electrodes. Working electrode (WE) is very sensitive to any change in analyte solution, provides the surface for the analyte to undergo reaction, when the potential is applied between WE and RE. The CE helps in completing the circuit by allowing the reaction, which is opposite to WE reaction, to happen. If an oxidation reaction happens at WE, reduction reaction will take place at CE, and vice versa. The RE is independent of the analyte and other ions concentration. Its potential is constant while measuring the potential of WE. By measuring the current of redox reaction, the analyte can be identified. The figure 4.13 represents the electrode system of the EC sensor. For the EC sensor system as shown in figure 4.13(a), the RE can be Standard Hydrogen Electrode (SHE), calomel electrode, silver-silver chloride, CE can be Gold, platinum and carbon electrodes, and WE can be Carbon, glassy carbon electrode (GCE).

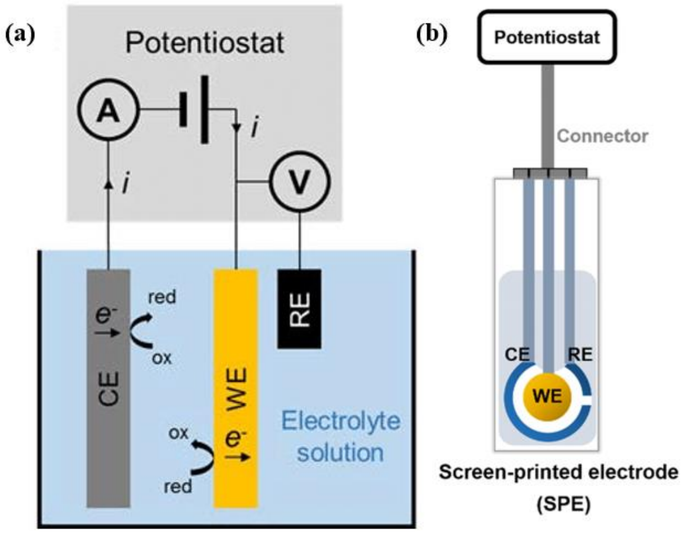


Figure 4.13. Three electrode systems used in electrochemical sensor (a) Combination of three distinct electrodes (b) Screen printed carbon electrode (all three combined)

The electrode shown in figure 4.13(b), is named as screen printed electrode, which is low cost, disposable, which are fabricated by printing the ink of carbon, silver, gold, and platinum on plastic (Flexible Polyester Film) or ceramic substrate. WE are generally printed by graphite or carbon (graphene, CNT) based ink, RE are printed by silver/silver chloride ink and CE is by carbon ink.

The EC sensor used to for various analytes such as hydrogen peroxide, glucose, urea, alcohol etc, which are adsorbed on receptors (nanomaterials, Graphene, CNTs metal oxides). They undergo redox reaction upon applying voltage, the resultant current (electrons released) is measured by transducer, which is characteristic property of a biomolecule under study. Then the current is quantified by using amplifier and recorder as shown below.

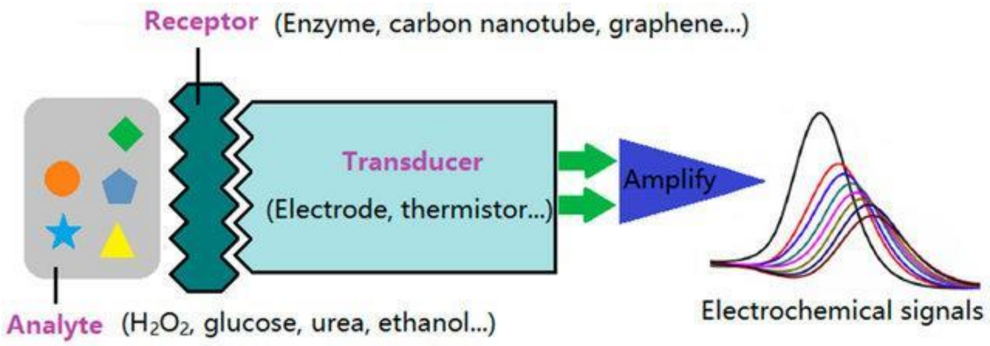


Figure 4.14. Electrochemical sensor components; Analyte, Receptor, Transducer and recorder

Applications of Electrochemical sensor for biomolecules

Glucose sensor in diabetes management

In EC sensor, glucose and oxygen react in the presence of nanomaterials or glucose oxidase (GOx) functionalized WE, and thus oxygen is consumed and hydrogen peroxide is produced (as shown in equation below). Further, the glucose concentration can be detected indirectly by electron transfer of oxygen at CE as shown in reaction.

WE: Glucose + O_2 + H_2O $\rightarrow$ Gluconic acid + H_2O_2

CE: $O_2 + 4H^+ + 4e \rightarrow 2H_2O_2$

Ascorbic acid sensor

Ascorbic acid (AA) is also called as Vitamin C, an essential nutrient and antioxidant required for the human body. Unfortunately, the human body cannot produce/synthesize this biomolecule, and hence it should be consumed by food and drugs. The deficiency of AA lead to scurvy, mental disorder, cancer, etc.

Similar to glucose, the AA can also be analyzed in EC sensor and the following schematic representation depicts the sensor mechanism of AA.

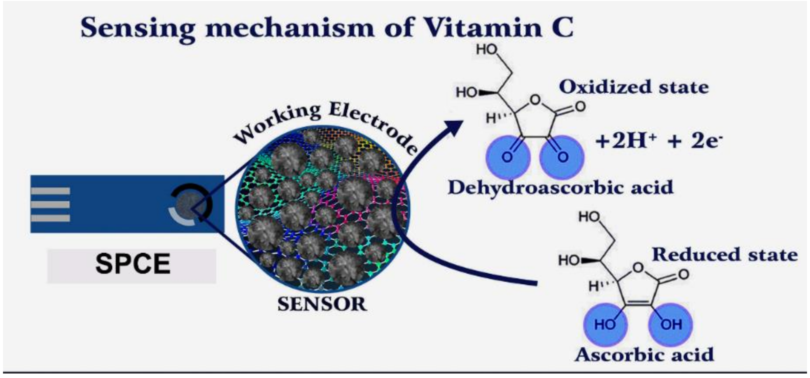


Figure 4.14. The SPCE is functionalized with nanomaterials and possible redox reaction of AA at WE.

VOCs sensor

Volatile organic compounds are the organic molecules having very low solubility in water and exhibit a high vapor pressure. They are liberated in industries such as pharma, biotech, paints, vanishes. Some examples of VOCs are Phosgene, benzene, ethylene glycol, formaldehyde, methylene chloride, tetrachloroethylene, toluene, xylene, acetone, alcohol, and 1,3-butadiene etc. These VOCs are very dangerous to health upon inhaling, which effects to the liver, kidneys, or central nervous system, even some VOCs are suspected or proven carcinogens. Further, the healthy individual's exhaled breath has major VOCs such as isoprene (12-580 ppb), acetone (1.2-1,880 ppb), ethanol (13-1,000 ppb), methanol (160-2,000 ppb) and other alcohols. Today, human exhaled breath analysis using gas sensors and e-noses (as shown below), is helping the diagnosing a wide range of diseases.

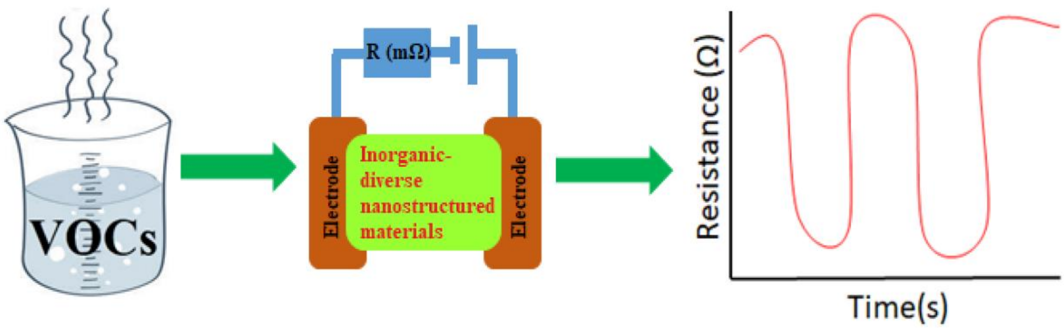


Figure 4.15. Schematic illustration of device based sensing of diverse nanostructures to volatile organic compounds (VOCs). [https://doi.org/10.3390/s21020633]

Electrochemical Gas sensors

Electrochemical gas sensors also called as electrochemical gas detectors, which are designed to identify and measure the quantity of the concentration of gasses like oxygen, carbon dioxide, carbon monoxide, hydrogen, NOx, SOx, POx, LPG, H_2S etc . These gases are produced from industrial emissions, vehicle exhaust and open burning of garbage waste, which needs to be monitored. Therefore the electrochemical gas sensors can be effective tool for analyzing them, as it consumes less power than other conventional gas sensors.

The schematic representation of working electrochemical has sensor with respect to CO is represented as follows. [https://doi.org/10.1016/j.sintl.2021.100116]

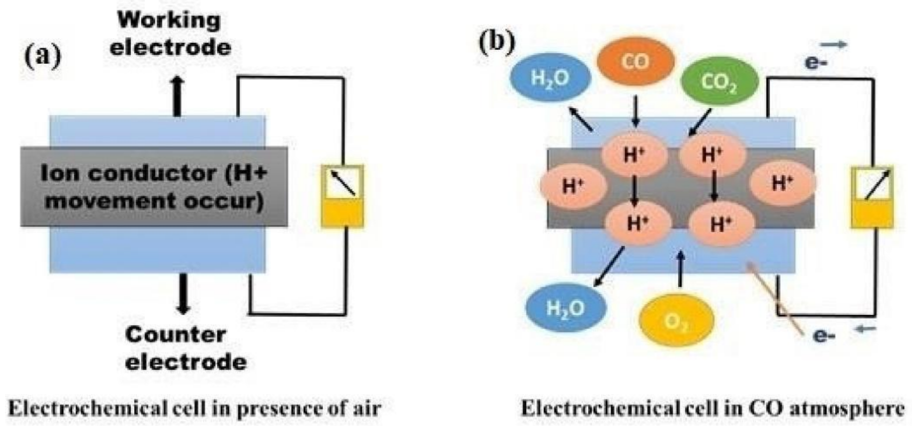


Figure 4.17. Schematic illustration of EC sensor (a) air , (b) carbon monoxide.

The EC gas sensor system consists of combination of two or three electrodes which are called reference, working, auxiliary/counter electrodes and ionic conductor between them as shown in figure 4.17. In this setup, the ionic conduction of the electrolyte, which in contact with WE and CE, complete the circuit. When gas molecules (CO) reacted with WE as shown in reaction below, **@WE,** $CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$: The electrons released at WE are made to pass through externally and the H^+ ion internally towards CE. By measuring the current flow, the type and quantity of gas sensor can be measured.

Model Questions:

Q. No	Questions	Marks	COs	BTL
1	Name the smart device that works with the help of radio frequency waves.	2	1	1
2	Express the significance of RFID in smart devices.	4	3	1
3	Describe the role of important components of RFID.	4	3	1
4	Distinguish the types of RFID.	4	2	2
5	Explain the role of IoNTs technology in advancing the engineering and medical field.	4	3	2
6	List the nanomaterials used in RFID for IoNTs technology.	2	1	1

7	Draw the structures of CNT and graphene.	4	2	3
8	Analyze the structural differences between CNT and Graphene.	4	2	3
9	Construct the CVD setup for the fabrication of CNT and elaborate the synthesis protocol with mechanism of crystal growth.	6	4	4
10	Categorize the two types of functionalized CNTs and summarize them with suitable examples.	6	1	4
11	List the properties of CNTs	2	1	1
12	Propose the synthesis protocol for making GO from graphite.	5	2	3
13	Describe the modified Hummer's method for the synthesis of rGO.	5	3	2
14	Recommend the protocol for converting graphene to graphene-NH_2.	2	4	4
15	Illustrate the physical/chemical functionalization of graphene with suitable example	4	1	2
16	Predict the product when graphene oxide is subjected to reduction in hydrogen environment.	2	2	3
17	Elaborate the chemical oxidative polymerization of aniline	4	2	2
18	Draw the various structures of PANI and identify the conducting polymer among them.	4	2	3
19	Explain the working principle of sensor with schematic diagram.	4	1	1
20	List the type of sensors	2	1	1
21	Explain the working principle of Piezoelectric sensor with schematic diagram.	4	2	3
22	List the important characteristics of Piezoelectric sensor.	2	1	1
23	List the applications of Piezoelectric sensor.	4	1	1
24	Demonstrate the working principle of electrochemical sensor	4	3	2
25	Highlight the role of three electrodes used in EC sensor	3	3	2
26	Elaborate the application of EC sensor sensor in diabetes management	4	4	4
27	Propose the possible structural change of ascorbic acid responsible for EC sensor signal.	2	3	3
28	Describe the working principle of Electrochemical Gas sensors	4	3	2