

# **Development of Palladium Based Nanocomposites for Functional Applications**

A dissertation submitted in the partial fulfillment of  
the requirement for the degree of

**Bachelor of Science**  
in  
**Chemistry**

Submitted by:  
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May, 2024

# DECLARATION

I declare that the thesis entitled “**Development of Palladium Based Nanocomposites for Functional Applications**” has been prepared by me under the supervision of **Dr. Shikha Wadhwa and Dr. Shilpi Agarwal** from **Department of Chemistry, School of Applied Engineering, University of Petroleum & Energy Studies, Dehradun, India.**



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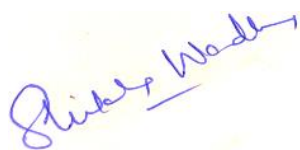
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This is to certify that, **Vasvi Kaushik** has prepared this project entitled “**Development of Palladium Based Nanocomposites for Functional Applications**” for the award of the degree of **B.Sc. (Hons) Chemistry**, under the guidance of Dr. Shikha Wadhwa and Dr. Shilpi Agarwal. She has carried out the work at the **Department of Chemistry, School of Applied Engineering, University of Petroleum & Energy Studies, Dehradun, India.**



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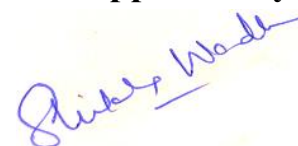
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## Abstract

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### Keywords:

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*Nanomaterial composites*

*Palladium nanoparticles*

*Synthesis*

*Characterization*

*Catalysis*

*Sensing*

*Biomedical applications*

*Synergistic effects*

*Technological challenges*

*Advanced materials.*

Nanomaterial composites have emerged as promising candidates for various functional applications owing to their unique properties and synergistic effects. One such important application is the detection of volatile organic compounds (VOCs) for various potential applications in the field of healthcare, environmental monitoring, indoor air quality management and so on. In this study, we focus on the development of Palladium based nanocomposites with carbon porous nano powder (CPN) and MXene, harnessing the exceptional characteristics of Palladium nanoparticles in conjunction with nanomaterials. The synthesis of these composites involves innovative methodologies tailored to achieve controlled morphology and enhanced properties. Through comprehensive characterization techniques, including spectroscopic analyses, we elucidate the chemical, environment and the crystal structure of the Palladium composites. Furthermore, we explore the performance of Palladium-Carbon Porous Nano powder (Pd-CPN) composite in the electrochemical detection of Isoprene, one of the volatile organic compounds (VOCs), released in the breadth and a biomarker of various diseases. The synergistic interplay between Palladium nanoparticles and materials imparts superior performance in these applications, showcasing the potential of these composites in addressing pressing technological challenges.

# Chapter 1

## Introduction

### 1.1 Volatile Organic Compounds (VOCs)

In the present times, VOC sensing holds significant importance as they detect (VOC) volatile organic compounds which are compounds with high vapour pressure and low water solubility. Paints, medications, and refrigerants are just a few of the man-made compounds that are used and created when making VOCs. Industrial solvents like trichloroethylene, fuel oxygenates like (MTBE) methyl tert-butyl ether and byproducts of water treatment processes like chloroform are examples of volatile organic compounds (VOCs). Petroleum fuels, hydraulic fluids, paint thinners, and dry cleaners are frequently made using volatile organic compounds (VOCs). VOCs are frequent pollutants found in groundwater.

VOC sensing is very important in many applications. The following important ideas, taken from the references given, help to clarify the importance of VOC sensing:

- **Healthcare:** Sensing of some volatile organic compounds released in human breath can be analysed as a biomarker for several diseases such as Lung cancer, Hypoglycaemia and so on. For example, ethanol, benzene, isoprene etc are released in human breath in very low concentration, however, the levels of these compounds show drastic increase or decrease during a disease and hence can be used as a biomarker for such disease.
- **Security and Well-Being:** By identifying potentially dangerous substances in the air, VOC sensors are essential for maintaining worker safety and protecting public health. They enable quick action to reduce hazards and stop exposure to dangerous VOCs by giving residents early warnings.
- **Environmental Protection:** By monitoring air quality and identifying volatile organic compounds (VOCs) coming from a variety of sources, including household goods, industrial activities, and vehicle exhaust, VOC sensors help to safeguard the environment. Identification of pollution hotspots, trend analysis of air quality, and development of air quality management policies are all aided by this monitoring.

- **Indoor Air Quality:** To detect the many volatile organic compounds (VOCs) that are present indoors, VOC sensors are crucial for monitoring indoor air quality. Because elevated VOC concentrations can cause health problems like headaches, nausea, and damage to important organs, this monitoring is essential. These sensors support the upkeep of healthy indoor environments by identifying and measuring VOCs.
- **Obstacles Associated with Cross-Sensitivity:** Although VOC sensors are important, they can react to gases other than the target VOCs, which presents a cross-sensitivity difficulty. This may result in erroneous measurements or false alarms.
- **Research and Development:** Current studies investigate novel materials and sensor architectures in an effort to improve the selectivity and accuracy of VOC sensors. In the realm of gas sensing technology, improving the accuracy and selectivity of VOC sensors is still a major objective to safeguard public health and enhance environmental monitoring.

In conclusion, VOC sensing is essential to maintaining worker safety, protecting the environment, protecting human health, and monitoring indoor air quality. Despite challenges like cross-sensitivity, the aim of ongoing research and sensor technology advancements is to improve the precision and dependability of VOC sensor for improved environmental and health outcomes. According to the sources cited, volatile organic compound (VOC) detection for sensing entails using a variety of detecting techniques in VOC gas sensors to identify and quantify volatile organic chemicals in the surrounding air.

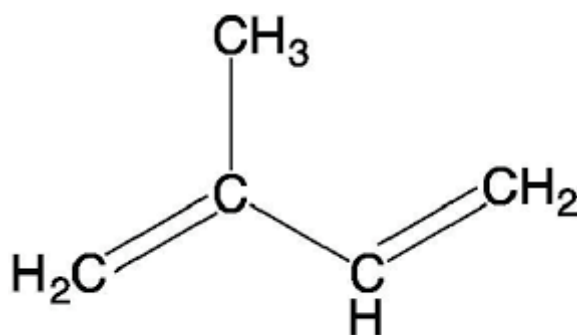
The following are important considerations for VOC sensing detection:

- **Mechanisms of Sensing:** Various detecting technologies, such as Photoionization Detection (PID is a), Metal Oxide Semiconductor (MOS), and Electrochemical Sensors, are utilised by VOC gas sensors to function. MOS sensors rely on variations in electrical conductivity, PID sensors ionise VOC molecules with UV light, and electrochemical sensors use redox reactions to provide electrical signals.
- **Interpretation and Analysis of Data:** In order to derive significant insights, it is necessary to analyse and analyse the substantial amounts of data generated by VOC gas sensors. To find patterns, trends, and abnormalities in VOC concentration levels, sophisticated

algorithms and methods for signal processing are applied. Instant alarms and messages are provided by real-time monitoring systems for proactive control of air quality.

- **Accuracy and Calibration:** Calibration is essential to guaranteeing the dependability and accuracy of VOC gas sensors. To enable precise measurements in real-world situations, manufacturers calibrate detectors to detect particular volatile organic compounds (VOCs) at established quantities. Over time, accurate detection and optimal sensor performance depend on regular calibration and maintenance.

## 1.2 Isoprene



**Fig 1. structure of isoprene**

With the chemical formula  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$ , isoprene, sometimes referred to as 2-methyl-1,3-butadiene, is a common volatile organic molecule. It is a colourless, flammable liquid that is made by a variety of plants, animals, and even people. The primary ingredient in natural rubber, isoprene finds extensive application in industrial manufacturing, mostly as a residue from the refining of petroleum. With a projected manufacturing rate of  $0.15 \mu\text{mol}/(\text{kg}\cdot\text{h})$ , isoprene is the most prevalent hydrocarbon detectable in breath within the human body. Numerous foods also contain small amounts of it. The biosynthesis of many different substances, including as terpenes, carotenoids, vitamins A and E, and the phenyl chains that make particular molecules, depends critically on isoprene. Approximately 95% of isoprene produced commercially is utilised to create cis-1,4-polyisoprene, a synthetic form of natural rubber.

Isoprene detection is significant for a number of reasons. It may be summarized as:

- **Effects on Health:** Isoprene is one of the VOC released in human breath along with other gases such as ethanol, methanol, benzene etc. However, the concentration of these gases is very low in human breath, they drastically change in the patient suffering from diseases such as Lung cancer, hypoglycaemia, liverfibrosis and others. Hence isoprene can be used as a potential biomarker for the detection of such diseases.
- **Industrial Processes:** Synthetic rubber and a number of other chemical compounds are produced using isoprene as a primary raw ingredient. Isoprene level monitoring is crucial for process optimisation and quality control in the rubber manufacturing industry.
- **Climate Change Research:** Temperature, sunlight, and vegetation type are some of the environmental elements that affect isoprene emissions from vegetation. Assess changes in isoprene emissions to learn more about the ways that climate change is affecting ecosystems and the environment.
- **Studies on biology:** Many different organisms, such as some bacteria, fungus, and marine algae, create isoprene. Understanding the metabolic processes and ecological functions of these organisms can be aided by the detection of isoprene.

The main organic component released into the atmosphere that is not methane is isoprene. It influences the generation of aerosols and ozone, controls atmospheric oxidation, and engages in interactions with the global nitrate cycle. For the purpose of comprehending atmospheric chemistry and climate, accurate monitoring of isoprene emissions is essential. In the atmosphere, isoprene has a brief lifespan of less than an hour. It has a high degree of volatility and reactivity, which can quicken reactions between materials in the atmosphere. To investigate the composition of the atmosphere and air quality, precise monitoring of this compound concentrations is required.

In conclusion, isoprene plays a critical role in climate, atmospheric chemistry, and human health. To understand its production, emission levels, and impact, measurement techniques that are sensitive, selective, and exact are necessary.

# Chapter 2

## Literature Review

### 2.1 Detection of isoprene

Isoprene detection research has advanced significantly in a number of scientific fields. In analytical chemistry, techniques like HPLC (High-Performance and Gas Chromatography-Mass Spectrometry (GC-MS) have proved crucial in precisely measuring isoprene levels in biological samples and air. In addition to these methods, new sensor technologies have been developed, such as surface acoustic wave (SAW) and electrochemical sensors, as well as platforms based on nanomaterials like graphene and carbon nanotubes. Techniques like FTIR, or Fourier transform and satellite-based observations have been extremely helpful in the field of remote sensing and atmospheric monitoring because they have shed light on the temporal and spatial distribution of isoprene emissions and clarified its role in atmospheric chemistry and climate. Isoprene has also garnered interest in the biological field, where it offers potential as a biomarker for a number of diseases. Computational modelling has made it possible to simulate isoprene emissions, air transport, and chemical interactions, which has complemented experimental efforts and contributed to a better understanding of the effects of the chemical on the environment and human health. Table 2.1 shows the literature review performed on the detection of isoprene.

**Specifically designed for isoprene detection, the development of palladium-coated carbon nanoparticle (Pd-CPN) sensors has shown amazing sensitivity and quick reaction times.**

**Table 2.1** The below given table gives a clear understanding of the existing composites in use.

| S. No | Authors                         | Title   | Key Findings  |
|-------|---------------------------------|---|---|
| 1.    | Viet Long Nguyen et al., [2010] | Chemical synthesis and characterization of palladium nanoparticles  | <ul style="list-style-type: none"> <li>• very sharp corners and edges of tetrahedral and octahedral Pd nanoparticles or others that were formed in the clustering and combination of the seeds of smaller particles.</li> <li>• PVP–Pd nanoparticles of cubic, octahedral, tetrahedral and spherical shapes with well-controlled size achieved by using ethylene glycol (EG) as reductant and various inorganic species were also fabricated</li> </ul> |
| 2.    | Hong Yuan et al., [2022]        | Palladium nanoparticles decorated MXene for plasmon-enhanced photocatalysis   | <ul style="list-style-type: none"> <li>• an effective separation and collection of localized surface plasmon resonance (LSPR)-induced hot charge carriers generated.</li> <li>• The Pd MXene shows approximately 2-fold enhancement of photocatalytic activity and excellent photostability under laser irradiation</li> </ul>  |
| 3.    | A.T. EzhilVilian et al., [2023] | Palladium nanoparticles anchored MoS <sub>2</sub> -MXene composite modified electrode for rapid sensing of toxic bisphenol A in aqueous media | <ul style="list-style-type: none"> <li>• prepared sensor showed excellent selectivity for the quantification of BPA even in the presence of electrochemically active interfering compounds such as drugs, pollutants, biological</li> </ul>   |



|    |   |  |   |
|----|---|--|---|
|    |   |  | substances, and some cations/anions.  |
| 4. | K. Le Van et al.,[2009]                               | Electrochemical formation of carbon nano-powders with various porosities in molten alkali carbonates   | <ul style="list-style-type: none"> <li>• Quasi-spherical” carbonaceous particles were obtained with average diameter comprised between 30 and 50 nm.</li> <li>• <a href="#">The crystallinity</a> and morphology of the powders were strongly influenced by the operating conditions, i.e. potential deposition, temperature of the molten carbonates, temperature of the drying process after washing.</li> </ul>  |
| 5. | <a href="#">Thanh Hoang Phuong Doan</a> et al.,[2021] | Palladium nanoparticle-decorated multi-layer Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> dual-functioning as a highly sensitive hydrogen gas sensor and hydrogen storage | <ul style="list-style-type: none"> <li>• nanocomposite also unveiled some extent of hydrogen storage capability at room temperature and 77 K, raising a possibility that it can dual-function as a hydrogen sensor and hydrogen storage.</li> <li>• The optimized Pd–Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanocomposite showed superb hydrogen-sensing capability even at room temperature with sharp, large, reproducible, concentration-dependent, and hydrogen-selective responses.</li> </ul> |
| 6. | Das et al.,[2015]                                     | Carbon Nanotubes Characterization by X-ray Powder Diffraction  | <ul style="list-style-type: none"> <li>• Complicated physico-chemical aspects and novel schemes to synthesize controlled featured carbon nanotubes have added new ambiguities to their characterizations and applications</li> </ul>  |

|    |                           |                                |   |
|----|---------------------------|--------------------------------|---|
|    |                           |                                | and these must be resolved on an urgent basis.  |
| 7. | F. Pacifico et al.,[2009] | Isoprene emissions and climate | <ul style="list-style-type: none"> <li>• volatile organic compounds (BVOCs) play an important role in <a href="#">atmospheric chemistry</a> and the <a href="#">carbon cycle</a>. Isoprene is quantitatively the most important of the non-methane BVOCs (NMBVOCs), with an annual emission of about 400–600 TgC.</li> <li>• plants emit isoprene and the relative importance of different environmental controls on isoprene emission</li> </ul> |

## 2.2 Materials for isoprene detection

Many materials have been thoroughly studied for their potential use in isoprene detection; these materials provide a range of sensing strategies based on unique physical and chemical characteristics. Because of their large surface area and remarkable electrical conductivity, carbon nanotubes, or CNTs, have been studied extensively. Researchers have been able to selectively adsorb isoprene molecules onto functionalized carbon nanotubes (CNTs), which has resulted in quantifiable changes in electrical characteristics and allowed for sensitive detection. Similarly, graphene has become a viable material for isoprene sensing due to its two-dimensional composition and high electron mobility. When modified graphene or graphene oxide (GO) sheets come into contact with isoprene, they change in electrical conductivity or optical characteristics, which makes it easier to identify isoprene. Because metal oxides are inherently sensitive to gas molecules, they have also been used, such as tin dioxide (SnO<sub>2</sub>) and zinc oxide (ZnO). Surface reactions are responsible for the electrical resistance changes that metal oxide-based sensors experience when exposed to isoprene.

Polymer films, such as polyethylene and polyaniline, can provide variety in sensing applications since they vary when exposed to isoprene vapour in terms of conductivity or

impedance. Using diverse materials for synergistic effects, metal-organic frameworks (MOFs) and nanocomposites represent novel techniques for selective isoprene detection. In addition, palladium (Pd) and palladium-based substances, which are well-known for their catalytic qualities and their attraction to unsaturated hydrocarbons, have been employed in isoprene sensors. These sensors, specifically Pd-coated versions such as Pd-CPN sensors, exhibit enhanced selectivity and sensitivity.

The nanomaterials used for isoprene sensing are as follows:

a) Palladium



**Fig. 2 Palladium**

Due to a number of its characteristics, palladium (Pd) is a highly desirable material for sensing applications. This is especially true for gas sensors, such as those used to detect isoprene. First of all, it exhibits exceptional catalytic activity, which is particularly noticeable in reactions involving unsaturated hydrocarbons. These characteristics are in line with the molecular makeup of volatile organic molecules such as isoprene. Palladium's catalytic ability allows it to efficiently mediate interactions between target molecules and the sensing substance, causing noticeable alterations in the sensor response even at low concentrations of the analyte. Moreover, palladium-based sensors respond extremely well to changes in their surroundings, even in the smallest variations in gas concentrations. Because of its increased sensitivity, isoprene traces can be found, which is important for applications where even minute amounts matter. This selectivity reduces interference from other species, improving the sensor's accuracy and dependability. Palladium's high surface-to-volume ratio surface reactivity makes it easier for target molecules to be adsorbed and desorbed, which speeds up reaction times and improves recovery. Its ability to work with nanomaterials increases its usefulness even further by enabling the development of customised sensor systems with improved functionality.

Additionally stable throughout a wide temperature range, palladium-based sensors are adaptable to a variety of operating circumstances found in real-world situations. Palladium is a desirable option for sensor manufacture because of its relative abundance and affordability when compared to other noble metals, especially for applications requiring large-scale production. All things considered, palladium's thermal stability, cost-effectiveness, sensitivity, selectivity, surfaces reactivity, and compatibility with nanomaterials with less cost and temperature stability.

b) Carbon Porous Nano powder



**Fig. 3 Carbon Porous Nano powder (CPN)**

A type of carbon material known as carbon porous nano powder is distinguished by its high porosity and nano particle size. These materials have special qualities and potential uses in a variety of disciplines because they usually contain an enormous surface area and an arrangement of pores that are interconnected at the nanoscale size. Because of its many characteristics, carbon porous nano powder is ideal for a wide range of sensing applications. First of all, as a distinctive feature, its high surface area-to-volume ratio is noteworthy, providing a large active surface for interactions with molecules of interest. This characteristic improves the kinetics of gas molecule adsorption and desorption, enabling quick and accurate detection.

Furthermore, the large number of gas adsorption sites that carbon nano powder's porous structure offers contribute to improved sensitivity and selectivity. Moreover, carbon Nano powder has a high electrical conductivity, which is advantageous for the creation of electrical sensors. Quantitative detection is made possible by the easy measurement of changes in the electrical characteristics of the Nano powder brought about by interactions with target analytes.

Carbon Nano powder is also frequently inexpensive, lightweight, and mechanically strong, which makes it useful for the production and use of large-scale sensors. Generally speaking, carbon porous Nano powder is a very promising material for sensing applications, especially in the detection of gases like isoprene in monitoring the environment, industrial safety, and healthcare diagnostics. These properties include its large surface area, porous structure, conductivity of electricity, chemical resistance, and versatility in functionalization.

#### c) MXene

MXene is a type of a two-dimensional (2D) transition metal that includes carbides, nitrides, and carbonitrides. It is well-suited for gas sensing applications due to its distinct characteristics. First of all, the large surface area of MXene materials is beneficial for gas interaction and adsorption. Target gas molecules can attach to a lot of active sites on this huge surface area, which improves sensitivity and makes it possible to detect minuscule quantities. Furthermore, MXenes have superior electrical conductivity due to their metallic composition, which enables the conversion of gas-sensing events into quantifiable electrical impulses. This characteristic makes it possible to create electrical sensors that can identify minute variations in conductivity brought on by the presence of particular gases, such as volatile organic molecules like isoprene.

MXene materials offer attractive options for gas sensing applications in a variety of industries, such as industrial safety, environmental monitoring, and healthcare diagnostics. This is due to their versatility and adjustable features. The special qualities of MXene-based sensors have great promise to solve difficulties in sensing or identifying a wide range of gases with excellent selectivity and sensitivity as research into these sensors advances.

#### d) Graphene based materials

With their exceptional conductivity, high surface area, and customisable electrical characteristics, graphene and its derivatives, such as graphene oxide (GO) and reduced graphene oxide (rGO), are perfect for sensing applications. Graphene-based sensors that interact with the target analyte can alter their resistance, capacitance, or optical characteristics to detect isoprene. Graphene-based isoprene sensors with excellent selectivity, low detection limits, and high sensitivity have been developed, according to several research. An In<sub>2</sub>O<sub>3</sub>/MoS<sub>2</sub> nanocomposite-based ultrasensitive isoprene sensor, for instance, showed a response of 1.8 to 100 ppb isoprene with a detection limit of less than 5 ppb.

Graphene can produce heterojunctions and improve sensing performance when mixed with other nanomaterials such as metal oxides (e.g., In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>) or transition metal dichalcogenides (e.g., MoS<sub>2</sub>). Graphene's synergistic effects with the supporting nanomaterials enhance stability, increase the number of active sites, and improve charge transfer.

In conclusion, graphene-based sensors present a viable method for the selective and sensitive identification of isoprene, opening the door to the creation of non-invasive diagnostic instruments for a range of medical disorders. Optimising sensor design, enhancing sensing materials, and verifying performance in practical applications are the main areas of ongoing study.

#### e) Carbon nanotubes

Carbon nanotubes (CNTs) have demonstrated significant promise in the development of extremely selective and sensitive sensors for the detection of isoprene, a biomarker for a number of diseases. CNTs are perfect for sensing applications because of their special qualities, which include high surface area, good conductivity, and tunable electrical characteristics. When the target analyte interacts with CNT-based sensors, changes in resistance, capacitance, or optical characteristics can be used to identify isoprene. In conclusion, CNT-based sensors present a viable method for the selective and sensitive identification of isoprene, opening the door to the creation of non-invasive diagnostic instruments for a range of medical disorders. Optimising sensor design, enhancing sensing materials, and verifying performance in practical applications are the main areas of ongoing study.

## 2.3 Research Gap

Although there have been major advancements in the field of isoprene sensing utilising palladium nanocomposites, there are still a number of important research gaps that need to be filled. First, more research is required to optimise the composition and structure of palladium nanocomposite materials for improved sensing capabilities. Although the sensitivity and selectivity of palladium nanocomposites have showed promise, more research should be done to optimise sensing efficiency by precisely controlling the size, shape, and distribution of the nanoparticles inside the composite matrix.

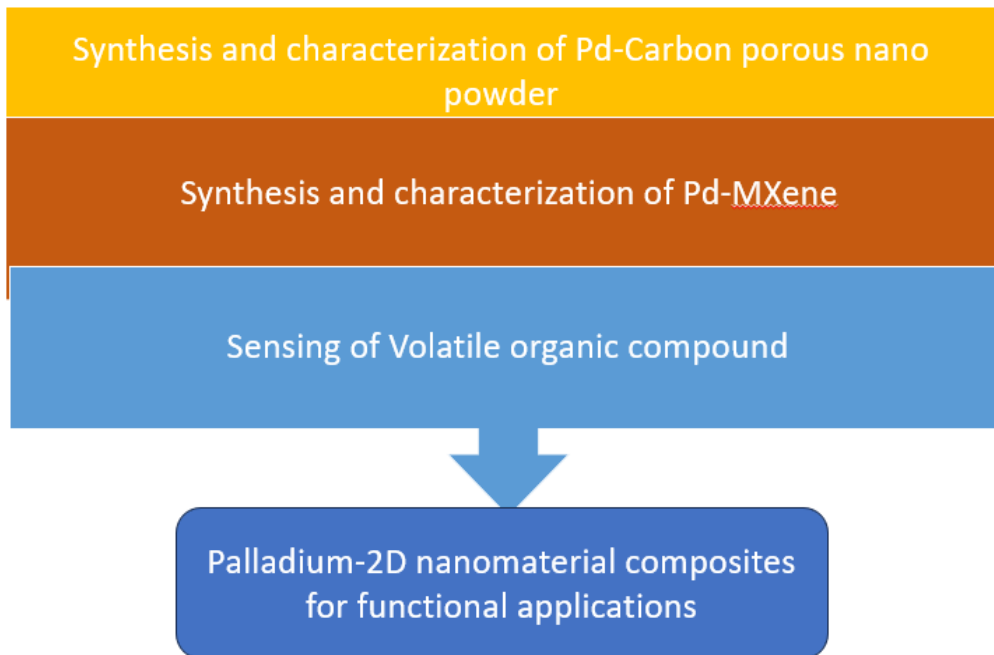
Secondly, a more thorough elucidation of the mechanisms behind the bonding between isoprene molecule and palladium nanocomposites is required. Gaining knowledge of the

particular adsorption and desorption processes at the surface of the nanocomposite could help to improve the stability, detection limits, and response times of the sensors.

Furthermore, thorough research on the long-term stability and dependability of isoprene sensors based on palladium nanocomposite is lacking, especially when it comes to real-world operating circumstances. It would be essential to look at how variables like humidity, temperature swings, and exposure to other gases affect sensor performance before implementing sensors in real-world industrial and environmental monitoring applications.

Ultimately, filling in these research gaps through multidisciplinary efforts involving environmental science, chemistry, materials science, and engineering may open the door to the creation of next-generation palladium nanocomposite-based isoprene detection sensors with enhanced sensitivity, selectivity, stability, and scalability.

## 2.4 Objectives of the project & timeline



## Timeline of the project

| Task                  | JAN | FEB | MAR | APR |
|-----------------------|-----|-----|-----|-----|
| Literature Review     | ←→  |     |     |     |
| Synthesis of Pd-MXene | ←→  |     |     |     |
| Characterizations     |     | ←→  |     |     |
| Synthesis Pd-CPN      |     |     | ←→  |     |
| Characterizations     |     |     | ←→  |     |
| Detection of VOCs     |     |     | ←→  |     |



# Chapter 3

## Experimental Details

### 3.1 Materials

#### Palladium Chloride

This was used for the synthesis of palladium nanoparticles. It is prepared by the reaction of chlorine with palladium metal at high temperatures. The purity of PdCl<sub>2</sub> was 99.9%.

#### Carbon porous nano powder

It was commercially purchased from Thermofisher and the pH range was 2.0-3.5 with moisture content 15%.

#### Maxphase

It was commercially purchased from Nano-Shell with purity of 99% and APS of 40-60 um. They are layered carbides and nitrides exhibiting combination of properties of metallic and ceramic materials.

#### Solvents used:

1. **Dimethyl formaldehyde (DMF)**

It was also purchased from sigma-Aldrich with vapour density 2.5 and vapour density 2.7 mmHg, assay 99.8%.

2. **Sodium Borohydride (formula), purity, company**

It was purchased from Sigma-aldrich.

3. **DI water**

#### PCB electrode

Company- Sigma Alrich

### 3.2 Methods

#### 3.2.1 Synthesis of Palladium Nanoparticles

- 10 ml distilled water is being taken in a beaker
- 1 ml Palladium precursor is added in the beaker
- Then it is kept for sonication for 30 minutes.
- It is kept on magnetic stirrer at 500 rpm for 1 hour

- Sodium borohydride is being added in the solution which is a reducing agent for metal ions.
- The nanoparticles formed are washed and centrifuged
- The solution formed is kept in the oven at 60 °C overnight
- The desired nanoparticles are obtained.

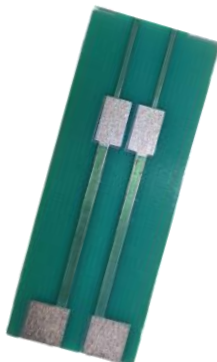
### **3.2.2 Synthesis of Pd- CPN Nanocomposite**

- 40 mg of CPN is weighed
- Add 20 ml of distilled water
- It is kept for sonication for 30 minutes.
- The solution is kept on magnetic stirrer at 500 rpm for 30 minutes
- Now, required amount of palladium nanoparticles are added (5, 10, 15 mg) as per requirements.
- Again, it is kept for stirring for 3-4 hours.
- Keep it in oven at 70°C overnight.
- The desired Pd-CPN nanocomposite is obtained.

### **3.2.3 Synthesis of Pd- MXene Nanocomposite**

- Take 20 ml of distilled water
- Weigh 50 mg MXene
- Add MXene in distilled water and sonicate it for 2 hours.
- Under sonication, add required amount of Palladium (10,20,30 mg) to above solution
- Again, it is kept under sonication and stirring for 2 hours
- Centrifuge and wash the solution with ethanol and water
- Dry the precipitate in hot air oven at 60°C.

### 3.2.4 Preparation of PCB (Printed Circuit Board) electrode



**Fig 4. Commercial Printed Circuit Board electrode**

Commercially manufactured PCB electrodes must be cleaned in order to provide a clean, repeatable electroactive surface and to remove surface contaminants before they can be used as electrochemical sensors. An insulating organic covering that covers untreated PCB electrodes frequently needs to be removed.

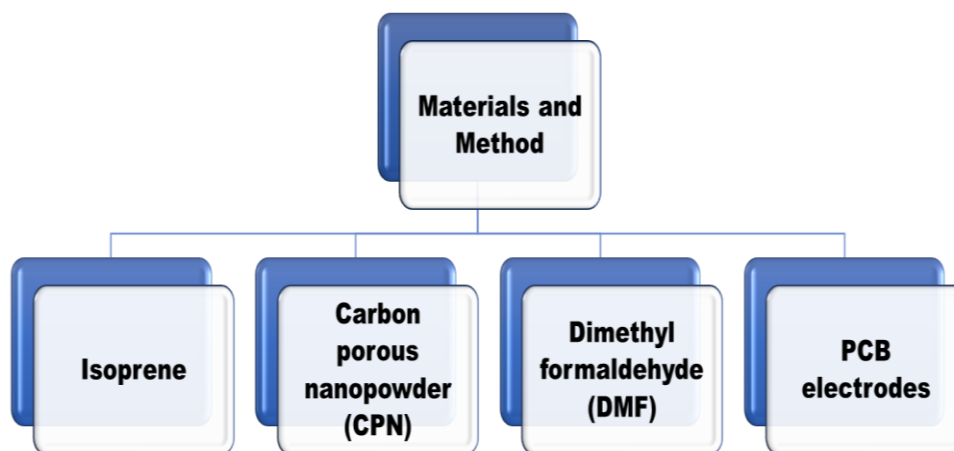
This is a general how-to for setting up a PCB electrode:

- **PCB selection:** Select a material for the PCB that is appropriate for your need. Usually, copper-layered PCBs made of fibreglass are utilised. The electrode's conducting surface is the copper layer.
- **Cleaning the PCB:** Give the PCB's surface a thorough cleaning to get rid of any impurities, grease, or dirt. To clean the surface, use a fresh cloth or tissue and a solvent (such as acetone or isopropyl alcohol). Before continuing, make sure the surface is totally dry.
- **Cutting and Shaping:** Using the proper instruments, like a saw or PCB cutter, cut the PCB to the required dimensions and form for your experiment.
- **Rinsing:** To get rid of any remaining etchant, give the PCB a thorough water rinse after etching. To avoid contaminating the working electrode surface, make sure the rinsing is done correctly.

- **Surface Activation:** In certain circumstances, the PCB's surface may need to be activated in order to increase conductivity and guarantee that electrodeposited materials adhere to it more successfully. Electrochemical techniques like cycling the voltage or applying the appropriate activation solution to the surface can be used to accomplish this.
- **Drying:** Before using the PCB electrode, let it air dry entirely after cleaning and preparing it. To expedite the drying process, you can use air drying or mild heat, but stay away from using too much heat as this could harm the PCB or any of its components.
- **Electrical Connections:** Lastly, make sure that the appropriate cables or connectors are used to connect the PCB electrode to your experimental setup. When you begin your electrochemical tests, make sure there are no loose connections or shorts.

A 5 microlitre solution of Pd-CPN was prepared by dispersing it into Dimethyl formaldehyde (DMF) which was used as solvent over an area of 28mm<sup>2</sup>. This solution is placed on deposition sites of PCB (Printed Circuit Board) electrodes in a sensing chamber. Both electrodes (Reference and working) are attached on the contact points of PCB electrodes. This is an electrochemical Reaction. To facilitate electrochemical sensing applications, PCB electrodes must first be cleaned to eliminate surface contaminants, and then they must be functionalized using a capture probe.

### 3.2.5 Detection of Isoprene

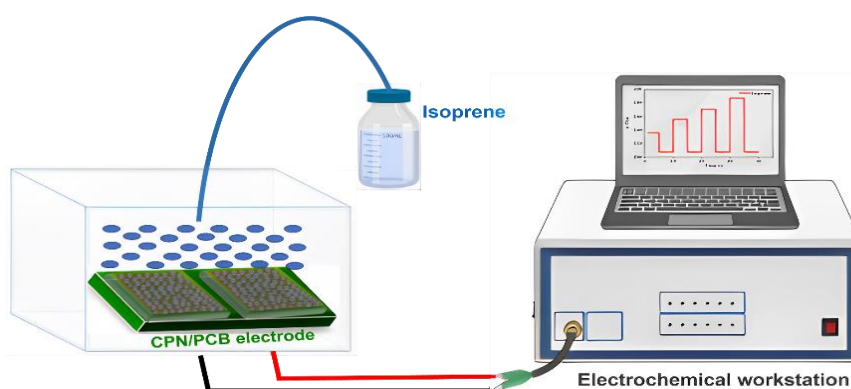


**Fig. 5 Materials and Methods used for electrode fabrication.**

As a sensitive and specific fluorescent probe, Pd-doped conjugated nanoparticles of polymers (Pd-CPN) can be utilised to detect isoprene, a biomarker for liver illness.

When compared to representative fluorophores, the Pd-CPN exhibits superior photostability and a comparatively large quantum yield. Comparing the Pd-CPN based sensor to conventional fluorescent probes reveals benefits including excellent sensitivity, selectivity, and photostability. It offers a viable method for creating metal-doped conjugated polymer nanomaterial-based portable breath analyser for clinical diagnostics.

In general, isoprene detection with a Pd-CPN sensor entails exposing the instrument to isoprene, monitoring its reaction, and interpreting the data to ascertain the isoprene concentration in the sample. According to the sensor layout and the analytical methods used, the specifics of the detection process may change.



**Fig 6. Sensing setup and working overview of sensor**

Impedance reading was recorded using Electrochemical Impedance Spectroscopy (EIS) on electrochemical work-station within the frequency ranging from 0.1 Hz - 0.1 MHz, signal amplitude of 10 mV. EIS is a potent approach for analysing the impedance of an electrochemical system. It is an effective method for determining the impedance of electrochemical systems, and it has a wide range of uses. The method is widely applied in many different domains, such as physical electrochemistry, batteries, and corrosion.

A custom-made sensing set-up (Fig. 6) which consists of an enclosed chamber with the provision of attachment of a tube leading to inflow of isoprene in gaseous form. The isoprene in liquid form is taken in a bottle to which a gas tube is connected. The gas tube is then inserted into the enclosed chamber which exposes the electrode to a fixed amount of isoprene. The change in electrochemical impedance with respect to time of isoprene exposure with the nanomaterial modified PCB electrode was measured in the concentration range of (0-134 ppb).

## Chapter 4

### Results and Discussion

#### 4.1 Characterization of Pd and Pd-CPN composite

**Materials- Pd, CPN and Pd-CPN were characterized by XRD and FTIR Spectroscopy**

##### 4.1.1 XRD Analysis

Analysing X-ray diffraction (XRD) is a useful method for understanding the crystalline material structure. X-ray diffraction (XRD) is a technique that uses X-ray radiation to measure the diffraction pattern that is produced. This pattern can be used to identify metal and mineral compounds, confirm the composition of the material, quantify crystalline phases, determine crystalline size, distinguish between amorphous as well as crystalline materials, and calculate the percentage of crystallinity in a sample.

A) XRD Spectra of Palladium nanoparticles

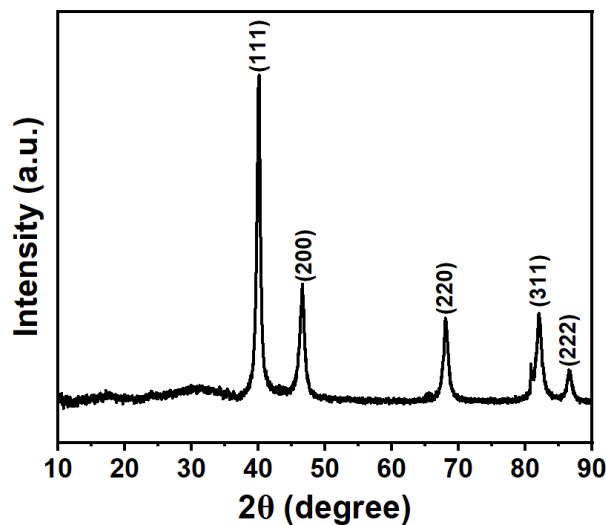


Fig.7 XRD Spectra of Pd nanoparticles

Palladium nanoparticles (Pd NPs) are confirmed to be crystalline by XRD analysis, which also sheds light on their structural makeup. Pd NPs' XRD patterns show distinct diffraction peaks, which point to clearly defined crystalline structures. The crystal structure of Pd NP can be ascertained by utilising the peak positions, which correlate to the distances between atomic planes in the crystal lattice. As an illustration, the face-centred cubic (FCC) crystal structure of palladium has distinct peaks in its XRD pattern at around  $2\theta = 40^\circ$ ,  $46^\circ$ ,  $68^\circ$ , and  $82^\circ$ , which correspond to the (111), (200), (220), and (311) planes.

B) XRD spectra of carbon porous nano powder is given below:

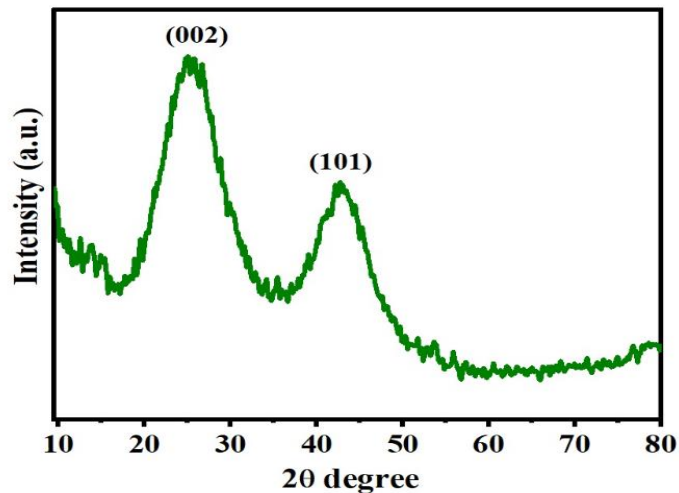


Fig. 8 XRD Spectra of carbon nano powder

This figure shows the XRD spectra of Carbon nano powder where peak at 002 and 101 resembles CPN. The peak at 002 is the prominent one. A graphitic structural characteristic was visible in the XRD patterns of Pc-CPN-2 materials at  $2\theta = 26.1^\circ$ . The hexagonal crystal system's graphitic plane spacing is characterised by its peak position.

To sum up, the XRD spectra of CPN-2 exhibit diffraction peaks that indicate the presence of a distinct crystalline structure. The positions and intensities of these peaks offer valuable information about the material's atomic arrangements and crystal structure. A higher degree of crystallinity than the less crystalline CPN-1 is shown by the sharp peaks.

C) XRD spectra of various concentrations of Pd-CPN in which concentration of Palladium varies whereas CPN remains constant is given below:

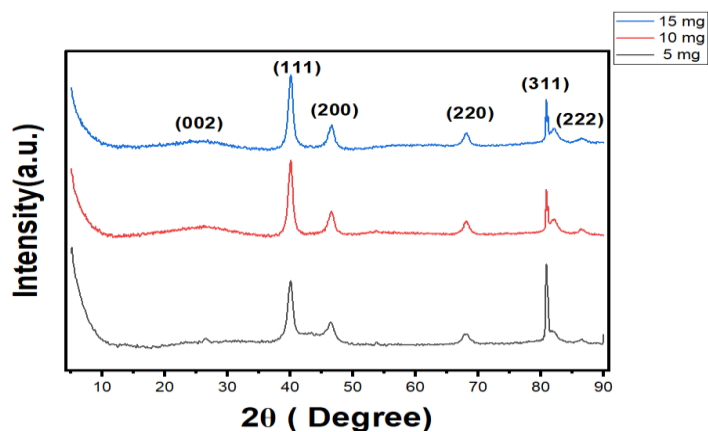


Fig.9 shows the XRD spectra of Pd-CPN where peak at 002 resembles CPN and the other peaks at 111, 200, 220, 311, 222 resembles Palladium

Pd-CPN materials usually show diffraction peaks in their XRD patterns, which are indicative of the palladium crystalline structure. Based on their locations and intensities, these peaks can be indexed to particular palladium crystallographic planes, such as (111), (200), (220), and (311). Additionally, depending on the degree of crystallinity and alignment of the carbon structure, diffraction peaks from the substrate of the underlying carbon nanoparticles may also be visible.

#### 4.1.2 FTIR Analysis

A strong analytical method for obtaining an infrared spectrum of the absorption or emission of a solid, liquid, or gas sample is Fourier-transform infrared spectroscopy (FTIR). The basis of FTIR analysis is a measurement of an object's infrared radiation absorption, which enables the identification of chemical compounds and their functional groups. FTIR analysis is frequently used to identify unknown compounds, validate compound identity, measure compound purity, and analyse molecular composition and structure in a variety of domains, including chemistry, pharmacology, geology, biology, and materials research.

D) FTIR spectrum of various concentrations of Pd-CPN in which concentration of Palladium varies whereas CPN remains constant is given below:

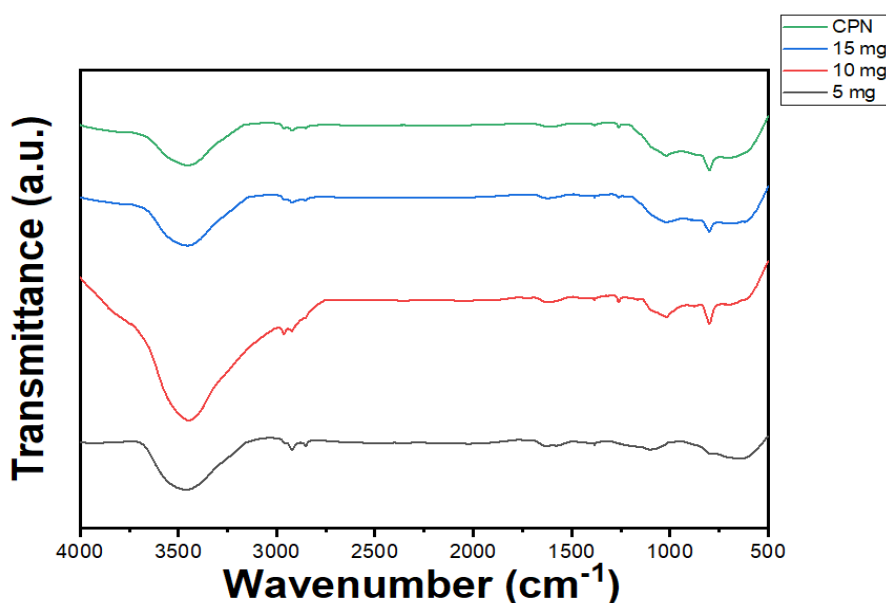


Fig 10. FTIR Spectra of Pd-CPN



The analysis above confirms the Pd-doped conjugated nanoparticles of polymers (Pd-CPN) have main absorption peaks in their FTIR spectra that correspond to particular functional groups and molecular structures. The vibrations linked to C-O stretching, C=C aromatic bonds, and C=N aromatic bonds are commonly observed in these absorption peaks, and they serve as indicators of the chemical moieties present in the Pd-CPN samples.

FTIR shows the -C=C- around  $1650\text{cm}^{-1}$  and OH peak at  $3450\text{cm}^{-1}$ .

The presence of C-O bonds within Pd-doped conjugated nanoparticles of polymers (Pd-CPN) is shown by the C-O stretching signal in their FTIR spectra, which is significant. Alcohols' extremely polar C-O bonds cause the C-O stretching vibration to typically appear in the range of  $1300$  to  $1000\text{ cm}^{-1}$  in their FTIR spectra. This region results in an intense stretching peak.

#### 4.2 Characterization of MXene and Pd-MXene by XRD and FTIR Spectroscopy.

E) XRD spectra of Mxene is given below:

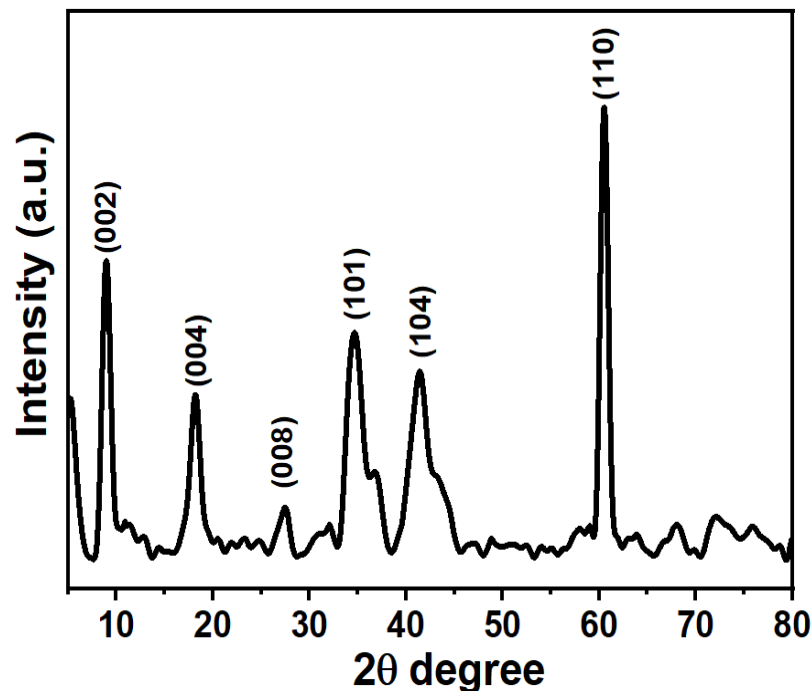


Fig.11 XRD Spectra of MXene

Figure shows the XRD spectra of  $\text{Ti}_3\text{C}_2$  MXene in which peak at  $9^\circ$  resembles to titanium whereas peak at  $35^\circ$  resembles to aluminium which is less in intensity as compared to the peak at  $9^\circ$ . The MXene crystal lattice's peak positions correlate to the distances between atomic planes, which can be utilised to ascertain the crystal structure. An instance of this may be seen

in the  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene XRD pattern, where the interlayer spacing between the MXene sheets is represented by a distinctive peak at about  $2\theta = 6\text{-}10^\circ$ .

F) XRD spectra of various concentrations of Pd-MXene in which concentration of Palladium varies whereas MXene remains constant is given below:

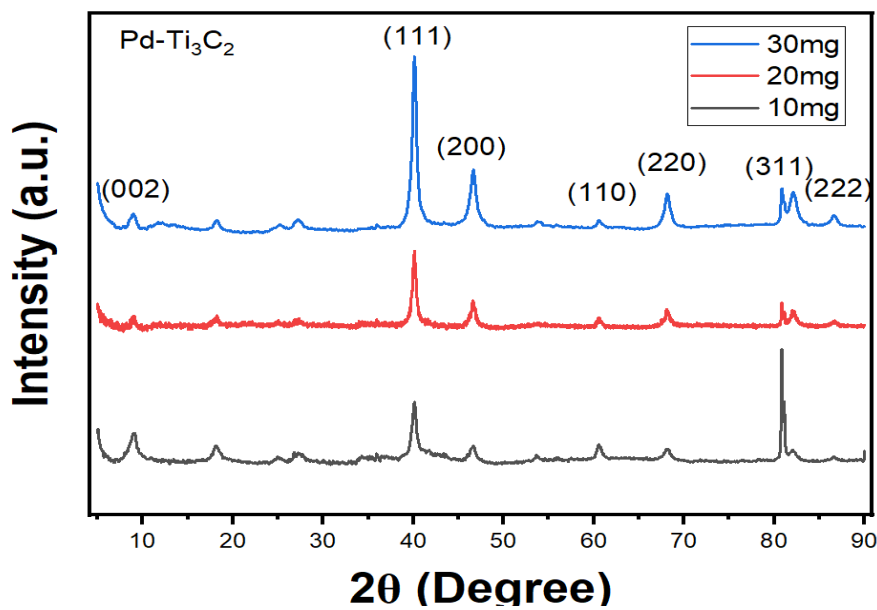


Fig. 12 XRD Spectra of Pd-MXene

The crystal structure of Pd-MXene can be ascertained by utilising the peak positions, which correlate to the distance between atomic planes in the crystal lattice. Pd NSs/MXene, for instance, shows distinctive peaks in the XRD pattern at approximately  $2\theta = 40^\circ, 46^\circ, 68^\circ,$  and  $82^\circ$ , which correspond to the (111), (200), (220), and (311) planes of the palladium face-centered cubic (FCC) crystal structure.

The size and degree of crystallinity of the Pd nanostructures can also be determined by observing sharpness and intensity of the diffraction peaks. Larger particle sizes and higher levels of crystallinity are indicated by sharper peaks. Moreover, in all the three samples the concentration of palladium is changed thus the intensity of palladium increases from graph A-C.

G) FTIR spectra of Mxene is given below:

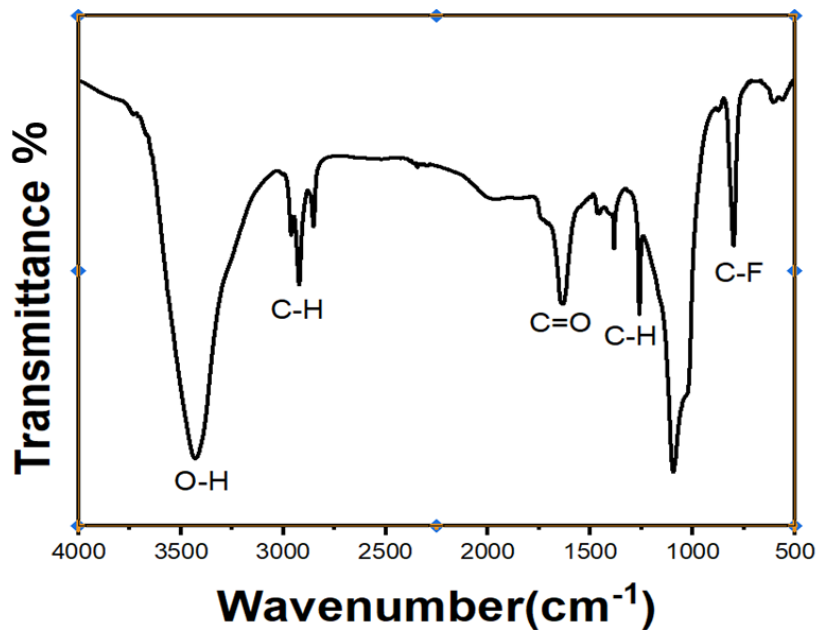


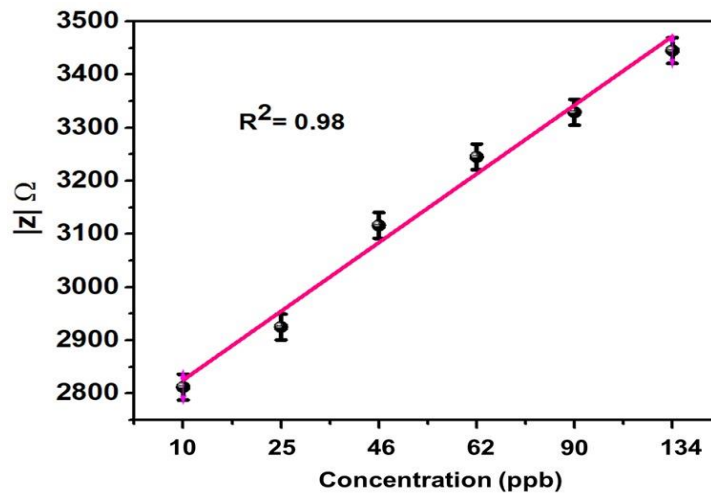
Fig. 13 FTIR Spectra of MXene

The following functional groups are frequently observed in FTIR spectra of MXene:

- **-OH stands for hydroxyl-** MXene's FTIR spectra usually show a distinctive peak at about 3434 cm<sup>-1</sup>, which corresponds to the -OH functional group.
- **C-O (carbon-oxygen):** In MXene FTIR spectra, a peak associated with C-O stretching vibrations is frequently detected in the 1300-1000 cm<sup>-1</sup> range.
- **Ti-OH (titanium-hydroxyl):** In the FTIR spectra of MXene, a peak at approximately 1480 cm<sup>-1</sup> indicates the presence of Ti-OH bonds. **Ti-F (titanium-fluorine):** Ti-F bonds are represented by a peak in the MXene FTIR spectra that is located at 950 cm<sup>-1</sup>.
- **Ti-O (titanium-oxygen):** The FTIR spectra shows a peak at roughly 642 cm<sup>-1</sup>, which indicates the presence of Ti-O bonds in MXene.

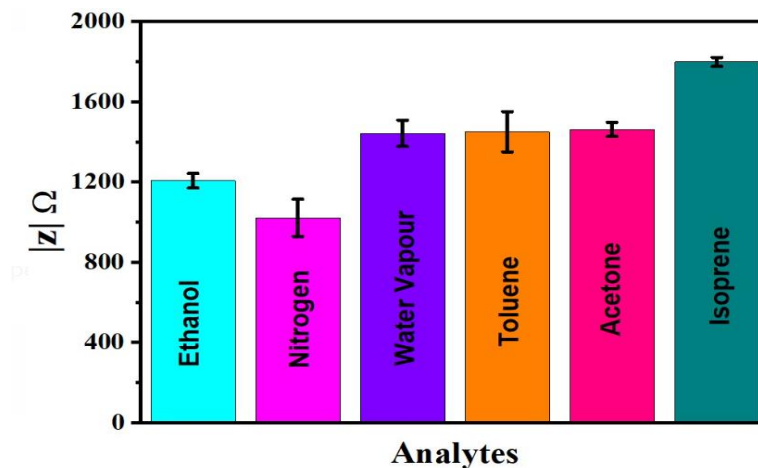
These were the various characterization graphs of CPN, Pd, Mxene.

Now, the results of VOC's sensing of isoprene are as follows.



**Fig.14** The above shown graph depicts isoprene sensing

As we can go through the graph, the concentration in ppb increases as the impedance increases respectively in which regression coefficient is 0.98 and the concentration of isoprene varies from 0-135 ppb. This graph is plotted between concentration and impedance  $|Z|$ . This was recorded through EIS on workstation.



**Fig.15** Selectivity graph of isoprene detection

This graph was plotted between impedance and various other VOC's present in human body. This clearly shows that the VOC sensor has highest selectivity for isoprene as compared to other volatile organic compounds. The impedance is highest for Isoprene in comparison to others.

# Chapter 5

## Conclusion and Future Prospects

### 5.1 Conclusion

Isoprene Detection was done with Pd-CPN sensor which was kept in an enclosed chamber with the provision of attachment of tube leading to gaseous form and impedance was recorded using electro-chemical impedance spectroscopy on Electro-chemical work station.

The results are listed below

**Result-** The Limit of Detection was found to be 10 ppb, where the response and Recovery time was 6 sec and 1 min respectively. It had good selectivity of Isoprene among Ethanol, Nitrogen, Water vapour, Toluene, Acetone

This work on the detection of isoprene is well compared with that reported in other studies. Our detection method resulted in the isoprene detection with 6 sec response time and 10% LOD at room temperature. This work demonstrates the potential of palladium-based nanocomposites for the detection of isoprene and hence, holds promise for the development of futuristic point of care device which may demonstrate rapid detection of isoprene in human breath correlated with the detection of diseases accurately.

### 5.2 Future Prospects

This work may be extended to the detection of isoprene using Pd-MXene and other such new materials. A comparative study between Pd-CPN, Pd-MXene and other new materials may be performed. Further direction may be the detection of other VOCs for the development of potential method for the detection of diseases.

We can extend it to other fields as well other than electrochemical sensing and development of futuristic point of care devices which may have commercial value.

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