

Electrostatically functionalized CVD grown multiwalled carbon nanotube/palladium nanocomposite (MWCNT/Pd) for methane detection at room temperature

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Abstract

By reducing the aqueous mixture of electrostatically modified multi-walled carbon nanotubes (f-MWCNT) and palladium (Pd) using NaBH₄, a nanocomposite was synthesized. The syllable structure of the f-MWCNT and f-MWCNT/ Pd nanocomposite was investigated by analytical tools FESEM and TEM respectively. f-MWCNTs matrix reinforced with Pd nanoparticles are utilized for sensing methane with its dilution varying from 0.5-100 ppm in air at room temperature (RT=27°C). The f-MWNT/Pd nanocomposite-based sensor for methane gas show several merits over conventional catalytic beads and MOS based sensors in context of reduced size, reduced power consumption and ease of fabrication. At room temperature, the nanocomposite's temporal electrical responses to methane were measured. It exhibited a response magnitude of ~20-45.71% with a small variation of ±2% towards 0.5-100 ppm methane. Furthermore, the responses were extremely reversible and repeatable, implying that it may be used to detect methane at ambient temperature. It has also been demonstrated experimentally that an excellent response time (≈ 20 s) and the recovery time (≈ 25 s) for these devices were recorded for methane. The influence of external temperature and humidity on the methane sensor was also investigated in order to assess its long-term stability and self-life. The results showed that very small change is observed over a wide of temperature from 25-70oC and that for %Rh from 20-90%. Therefore, the reported methane sensor absolutely demonstrated long-term stability at ambient conditions and hence, these devices can prove to be ideal for methane leakage detection for practical real time applications. A sensing mechanism by which methane is detected by f-MWCNT/Pd nanocomposite is also elaborately discussed.

1. Introduction

Methane is a colourless, odourless, highly combustible gas found in large quantities in nature. It is generated when natural materials decompose and is found in landfills, marshes, septic systems, sewers, and as a result of a variety of human activities, including coal mining. It's one of the most potent greenhouse gases. Methane is a very stable gas in general, but it is very explosive when mixed with air at a concentration of 5-14%. Coal mines pollute the environment by releasing methane into the atmosphere. Such pollutants have the potential to harm the ecosystem as well as human health. As a result, methane monitoring and its remediation is essential to protect public health because it is constantly discharged into the atmosphere.

As a consequence, there is a high necessity for user-friendly and environmentally acceptable sensing systems for on-the-spot, real-time detection of methane emissions, which are extremely hazardous to the environment and human lives. By far, numerous research on methane sensors including MOS gas sensors, photoacoustic-based gas sensor, graphene based gas sensor and SnO₂-based gas sensor have been published. However, these types of sensors have their own limitations like high power consumption, require continuous Ac supply, poor response and long recovery times etc. MWCNTs are widely used as sensing material for detection of various gases. The exceptional characteristics of MWCNTs including high aspect ratio, highly sensitive and fast recovery, made it a potential candidate for detection of

methane gas at ppm and sub-ppm levels. These characteristics are prerequisites to improve the interaction between methane and MWCNTs. However, pristine MWCNT have a tendency to agglomerate due to their strong sp² bonding in their hexagonal network. The agglomeration morphology of MWCNT will restrict their efficacy as a gas sensor. Alteration or functionalization of MWCNTs with various functional group is one way to overcome this shortcoming. Moreover, electrical properties of MWCNTs are sensitive towards chemical modifications by functional groups attached onto their surface.

For detection of methane leakage in air, Fedorenko et al. [1] suggested MOS gas detectors fabricated using Pd/SnO₂ nanoparticles. A sol–gel process was used to make semiconductor detectors based on nanosized Pd-doped tin dioxide. By filling MWCNTs with VO₂, Chimowa et al [2] improved methane gas detecting characteristics. MWNTs are filled with vanadium metal and then oxidized using a simple capillary process. At ambient temperature (293 K), the methane gas response time improves from 138 s (in V₂O₅) to 16 s (in filled MWNTs), while the recovery times decrease from 234 s to 120 s, respectively. At RT, Janudin et al. [3] created a carbon nanotubes-based gas sensor for detecting methane gas. The CNT was functionalized with an amide group and labelled as CNT-amide using the Fischer esterification procedure. Humayun et al. [4] demonstrated a highly sensitive, low-cost distributed methane sensor system (DMSS) for persistent monitoring, recognition, and detection of methane leaks in natural gas infrastructure such as transmission and distribution pipelines, wells, and production pads. The methane sensing element, a major module of the DMSS, is made up of a metal oxide nanocrystal (MONC) functionalized MWCNT mesh that, when interacting with lower concentrations of methane, exhibits a higher relative resistance change. Hannon et al. [5] used an array of sensors and principal component analysis to address the sensitive detection and discrimination of environmental gases such as methane, NH₃, SO₂, and CO (PCA). A 32-element chemiresistive array of sensors was constructed using nine different sensor materials, including seven different types of modified SWCNTs and two different polymers. PCA results demonstrate that the chemiresistor sensor chip has excellent discriminating ability in the 1–30 ppm concentration range. Bezdek et al. [6] described a chemiresistive sensor made of single-walled carbon nanotubes and a molecular platinum-polyoxometalate complex that is known to mediate methane oxidation near ambient conditions. It is demonstrated that the composite is a robust sensor that functions at RT, has air and moisture stability, and methane selectivity. The results indicate that techniques from molecular methane oxidation can be used to create low-power, low-cost, possibly distributable sensors for selective methane detection. Kathirvelan et al. [7] used MWCNTs as the sensing element to demonstrate a sensor for detecting and quantifying methane. To make the chemiresistive sensor element, silver electrodes were inkjet printed on a glass substrate and then brush coated with MWCNT. The sensor's sensitivity (the increase in resistance caused by analyte exposure) increases linearly with concentration of methane, with a maximum sensitivity of roughly 20% recorded for 160 ppm of methane. Chakraborty et al. [8] demonstrated that sensors based on Fe doped SnO₂ can detect methane and butane (primary components of CNG and LPG, respectively) at temperature 350°C. However, at 425°C, the same sensors may detect butane preferentially. Anas et al. [9] proposed developing a mine gas detection system composed of gas detecting sensors, a wireless network provider, and a microprocessor. MQ-4 and MQ-7 sensors are used to detect methane and CO, respectively. These sensors

are linked to an Arduino board, which is linked to an LCD display that displays the proportion of methane and CO on a daily basis. Mondal et al. [10] investigated the methane gas sensing activity of ZnO nanoparticles (average diameter 150–200 nm) synthesized on a Si/SiO₂ substrate using a thermal annealing technique. The sensor response was investigated for various methane gas concentrations (0.1-1%) and operation temperatures ranging from 70-200°C. The ideal temperature range was clearly between 150-200°C, with a sustained magnitude of sensor response as high as 75%. Mishra et al. [11] used silver and carbon nanotube films to fabricate and evaluate a surface plasmon resonance-based fibre optic methane sensor. The sensor can detect gas concentrations of up to 100 parts per million (ppm).

Most of the commercially available methane sensors are high temperature MOS based sensors require a micro heating element and hence continuous Ac supply for their operation. A versatile, spill-proof, contaminant-free, non-chemical technique based on corona-aided electrostatic charging for modification of MWCNTs has been adopted to attain this critical goal. In this technique, strong electric fields (\approx 9-13 kV) were used to simultaneously functionalize and deposit MWCNT films in ambient conditions, and the effects of electrostatic corona charging on the characteristics of MWCNT films were examined using various analytical characterization tools. By reducing their aqueous mixture in NaBH₄, a nanocomposite of f-MWCNT/Pd was synthesized. In addition, the electrical resistance of the f-MWCNT/Pd nanocomposite films has been carefully examined and characterized in response to their exposure to methane gas concentration. In a sealed test chamber of known volume, the gas sensing properties were investigated at RT under a pressure of 1 atm. The f-MWCNT/Pd nanocomposite films showed excellent methane sensitivity and selectivity, as well as quick response and recovery times.

2. Experimental

2.1. Chemicals & consumables

Chemicals and consumables for cleaning substrates and laboratory glasswares, such as acetone and ethanol etc. were procured from CDH Pvt. Ltd. The Ted Pella industrial grade conductive silver paste was obtained from an electronic component shop in the local market. Navyug Air Products in Noida, India provided the zero-air cylinder utilized in the experiment. For investigations, based on methane detection, a 2 kg canister of methane with a regulator valve is employed.

2.2. Synthesis of the f-MWCNT/Pd nanocomposite

To synthesize functionalized MWCNT (f-MWCNT), CVD grown MWCNT were electrostatically functionalized with high voltage discharge according to a well-defined protocol, followed by its investigation using FT-IR and Raman Spectroscopy to characterize the structural properties of the as-prepared f-MWCNT, which are described in detail elsewhere [12]. By reducing a mixture of f-MWCNTs and Pd salt, the f-MWCNT/Pd nanocomposite was obtained. f-MWCNTs (1.0 mg/mL) and palladium chloride (0.75 mg/mL) were typically mixed together in DI water using magnetic stirring. 5 mL of aqueous NaBH₄

(0.01 M) solution was added dropwise into 10 mL of the mixture for 30 minutes under ultrasonic treatment to reduce Pd²⁺.

2.3. Morphological analysis of f-MWCNT/Pd nanocomposite

The surface syllable structure and chemical composition of the sensing f-MWCNT/Pd nanocomposite were examined using a Zeiss scanning electron microscope (SEM) EVO 18. A JEOL JEM 2100 TEM system with a 200 kV accelerating voltage was used for the studies. Ultrasonically grinding and dispersing the granular specimens in ethanol for 5 minutes produced the specimens appropriate for TEM analysis. Finally, the particles were carefully put on a copper grid with an amorphous carbon sheet serving as a support.

2.4. Fabrication of the gas sensor electrostatically

The as prepared aqueous dispersion of the f-MWNTs/Pd nanocomposite was ultrasonicated for 2 hours, then centrifuged for 10 minutes at 2000 rpm, the liquid was pipetted off, and the remaining granules were filtered using a glass funnel and filter paper, and then dried at 60°C in a glass petri-dish to produce blackish brown granules that were finely ground before deposition. The corona-aided electrostatic charging was employed to deposit f-MWCNTs/Pd based nanocomposite onto the surface of thin teflon fibres (dia ≈ 250 μm and length ≈ 7-9 mm). The detailed description of the electrostatic corona aided thin film deposition is clearly demonstrated in the supplementary material provide elsewhere [12]. Before deposition, a dielectric slurry prepared from a saturated solution of PVAc in acetone was prepared and applied to the surface of teflon fibres to ensure reliable adhesion. The films were then left to dry in the open air for 10-12 hr. A piece of teflon wire with f-MWCNT/Pd nanocomposite coating is soldered to a piece of PCB, and external connections are prepared with Ted Pella industrial grade conductive silver paste. As a consequence, a methane-gas sensing device based on f-MWNT/Pd nanocomposite coated onto thin teflon wire was developed.

2.5. Experimental setup to measure the sensing response of f-MWCNT/Pd nanocomposite thin films to methane

Changes in the electrical conductance of f-MWCNT/Pd nanocomposite thin films when exposed to methane gas in a two-pole configuration under ambient circumstances are used to detect methane. The gas sensing experiments were carried out in a sealed test chamber with a known volume of 1000 mL at RT and 1 atm pressure. MFCs were utilized to control gas flow and concentration (Digital MFC: Horiba Multi Gas Digital Mass Flow Controller SEC-Z500X and Digital Read Out cum Control Unit PE-D20). The ultra-pure and dry zero air with a humidity percentage < 0.1 % was chosen as the carrier gas for purging methane into the sealed test chamber. The concentration for methane was maintained between 0.5-100 parts per million (ppm) (0.0005-0.1 ml per 1000 ml of zero air) using a three-way check valve and a controlled flow rate of zero air at 1000 ml/min. The valves were appropriately regulated and managed, allowing the sensor to be exposed in the closed test chamber to a mixture of clean zero air and methane gas while maintaining a constant pressure and flow rate. Data was taken 5 min after the target gas was

put into the test chamber to ensure proper dispersion and mixing of the target gas within the test chamber. The temporal responses of the variation in the electrical resistance of the sensing film was recorded using a computer-aided workstation coupled to a Keithley 6514 high precision electrometer via USB-GPIB interface. The experimental setup used for gas sensing investigations is depicted schematically in Fig. 1. The change in electrical resistance of the sensing film, % S, or sensor response of the f-MWCNT/Pd nanocomposite film to methane gas is calculated using Eq. (1) [13,14].

$$\%S = \left[\frac{R_{Max} - R_0}{R_0} \right] \times 100 \quad (1)$$

where R_0 (k Ω) is the base value of electrical resistance in air (in absence of methane)

R_{Max} (k Ω) is the steady-state electrical resistance value of the sensing film in response to the target gas

Response time τ_{Res} (s) is the time taken by the sensor to reach 90% of its steady-state electrical resistance value

Recovery time, τ_{Rec} (s) is the time taken by the sensor to retrieve back to 90% of its electrical resistance base value, i.e. R_0 (k Ω).

The gas sensing test chamber, as stated above, was flushed with dry zero air before being exposed to target gas to eliminate interfering effects on sensor efficacy caused by environmental humidity.

3. Results And Discussions

3.1. SEM Micrographs

The field enhanced scanning electron microscope (FESEM) images (Fig. 2) show swirled and bundled morphology of f-MWCNTs.

3.2. TEM Micrographs

Fig. 3 show the TEM micrograph of f-MWNT/Pd nanocomposite. The palladium nanoparticles are well disseminated in the f-MWNTs matrix, as can be seen. Pd particles with an average size of 10-15 nm make up the black dots.

3.3. Electrical measurements of sensor's gas sensing performance

The variation in the electrical conductance of the sensing film with its exposure to methane was observed and temporally plotted to examine the sensor response. The base value of the electrical resistance of f-MWCNTs/ Pd based sensing devices is typically found out to be 35 ± 2 k Ω in zero-air under ambient environmental conditions. All of the electrical observations were conducted at RT and at a pressure of 1 atm.

3.4. Selectivity studies on f-MWCNT/ Pd nanocomposite based sensor

It should be noted that a gas detector must have specificity in addition to high sensitivity in order to be useful for real-time applications. A MWCNTs-based gas sensor can achieve astonishingly high responsivity and specificity by customizing or grafting MWCNTs with a sensitive chemical or molecular group or ion that can promptly sense the target gas. The simplicity with which MWCNTs may be tailored distinguishes them from other materials and sensor development methodologies such as electrochemical sensing, MOS-based sensing, and infrared absorption sensing. The technique is particularly selective and irresponsive to other standard chemical interferences due to the unique interaction and redox reaction among methane gas and f-MWCNTs/ Pd nanocomposite. The gas sensing characteristics of the as-prepared f-MWCNT/Pd sensors were examined at RT by exposing them to a variety of gases at 100 ppm concentration. We studied and compared the sensor responsivity to the gases that are predicted to be major interferences to the methane sensor, as shown in Fig. 4, viz. CO, IPA, NO₂, NH₃, C₂H₅OH, Benzene, Acetone, CO₂, and so on. A maximum sensor response of 45.71 % over all target gases confirms the sensor's outstanding selectivity and sensitivity to methane over other vapors and gases. Because of their strong methane selectivity, these sensors did not require scrubbers to remove potential interferences in order to achieve acceptable accuracy. The f-MWCNT/Pd nanocomposite film's selectivity for methane detection is mostly owing to the rolling framework of MWCNTs, which increases the aspect ratio of the sensor and speeds up gaseous adsorption on the sensor surface [15]. Furthermore, the presence of many imperfections and impurities, in addition to reactable oxygenation sites attached to the sidewalls of MWCNTs, promotes charge transference between methane molecules and the sensor surface [16]. The exceedingly weak interaction of target gases on f-MWCNT sensing surface accounts for the poor sensing response for other gas molecules. The energy of the lowest unoccupied molecular orbit (LUMO), the quantity of gaseous analyte on the detecting surface, and the operating temperature altogether impact the fundamental parameters of a gas sensor [17]. A gas sensor serves as the energy source. As the target gas's LUMO energy falls, so does the energy required for the redox reaction, enhancing sensor responsiveness [17]. To put it another way, at RT, methane has the lowest LUMO energy of any of the target gases. According to the observations, the RT f-MWCNT sensor is highly specific and responsive to methane.

3.5. Sensitivity & reproducibility studies on methane sensor

The sensor's dynamic effectiveness is demonstrated in Fig. 5 by exposing the f-MWCNT/Pd nanocomposite-based sensing film to methane concentrations ranging from 0.5 to 100 ppm at RT. Surprisingly, when exposed to varied ppm levels of methane, the sensor displayed great sensitivity. When exposed to methane gas, the electrical resistance of the sensor increases dramatically due to methane molecule absorption on its surface. Similar results were achieved with randomly selected samples throughout multiple test cycles, with just a $\pm 2\%$ variation in sensitivity. It's worth mentioning that, as shown in Fig. 5, the time it takes for the resistance to equilibrate for methane varies between 20-25s depending on the concentration of methane gas. Fig. 6 depicts the percentage increase in electrical resistance of the f-MWCNT/Pd nanocomposite film as a function of methane concentration. As the

methane concentration grows from 0.5-100 ppm, the electrical resistance of the sensor film rises from 20 to 45.71%. This demonstrated a significant boost in system responsiveness as compared to commercially available MOS-based methane detectors. As demonstrated in Fig. 5, forceful flushing of dry zero air is utilized to expel and banish chemi-assimilated methane residues from the surface of the f-MWCNT/Pd nanocomposite film, causing its electrical conductance to recover to near-base value. As a result, it is repeatable and reusable.

3.3.3. Stability and self-life investigations on methane sensor

Periodic inspection for 30 days was used to assess the stability and shelf-life of the present methane sensor. Throughout the testing time, the sensor was constantly exposed to the ambient environment. As shown in Fig. 7, typical response curves of a sensing test to demonstrate the sensor's inherent stability characteristic for 100 ppm methane at RT were performed over 30 days, demonstrating the sensor's long-term stability and self-life. The dynamic response of the sensor is illustrated in the inset of Fig. 7, with no notable change in response and recovery rates between day 1 and day 30. The fabricated f-MWCNT/Pd nanocomposite sensor's high-performance methane detecting characteristics provide cutting-edge technology for toxic methane gas in the mining, home, and commercial sectors.

3.3.4. Humidity and temperature tolerance studies on methane sensor

The two key concerns for different gas and chemical sensors, namely electrochemical sensors, MOS-based sensors, IR-based sensors, and colorimetric sensors, are environmental humidity and temperature. Our sensor's humidity and temperature-dependent tolerance has been thoroughly examined. Although the humidity and temperature of the surrounding environment have a substantial impact on sensor performance, this is a well-known but correctable issue. The sensor responsivity for 100 ppm of methane was monitored and investigated for relative humidity (%RH) in the range 35-90% at RT and operating temperature range 30-75°C for real time practical applications. The temperature and pressure of the system also have an effect on the %RH. The interferent to sensor performance under consideration in this study is % RH, and the temperature was held constant for a proper assessment. The ambient humidity and temperature were measured using a commercial Acurite Pro Accuracy Indoor Humidity & Temperature Monitor with a sensitive probe. All experiments were carried out in a digital microprocessor-controlled humidity chamber (REMI SC-10 Plus) with precisely regulated temperature and humidity controls and a dual display PID microprocessor-controlled double walled thermally insulated oven with electrical feedthrough to investigate the effects of humidity and temperature on f-MWCNT/Pd nanocomposite-based methane sensor. To lower the % RH below the ambient level, silica gel was used. Environmental dampness, on the other hand, has a major impact on sensor performance. In the practical humidity range of 35-65 %RH, a relatively steady sensor response with a variance of roughly 0.001% for methane was measured, as shown in Fig. 8. Although carbon nanotubes contain both electrons and holes, they are most typically considered as a p-type semiconductor [18]. Because CNTs are hydrophobic, they interact with water molecules on a microscopic level [19]. Surface functional groups such as -OH or -COOH are formed as a result of the adsorption of H₂O molecules on the surface of CNTs. Because the p-

bonds between nanotube walls are sp² hybridised, water molecules adsorb on the surfaces of CNTs or between CNT walls, with electric charge transference recognized as a chemical process. H₂O molecules are adsorbed on CNT surfaces when exposed to dampness. The amount of adsorption is determined by the %RH. Because of the shift in electrical potential, electrons transfer from H₂O molecules to CNTs during adsorption. Rising humidity, as seen in Fig. 8, raises the electrical resistance of the sensor, which continues until the % RH reaches 70-80 %. Electrons migrating from H₂O molecules to CNTs recombine with majority carriers (holes) in CNTs, reducing the availability of holes in CNTs and hence decreasing the electrical conductance of the sensor. H₂O molecules have a critical role to play in electron donation. The sensor's electrical resistance's inclination to decrease with rising humidity over a particular %RH can be linked to two mechanisms: To begin with, the number of electron carriers increases as the quantity of electron impurity in CNTs increases. At higher RH levels, electrons become the predominant carriers in CNTs, transforming them from p-type to n-type. As the amount of adsorption generated electrons grows, the electrical resistance of the sensor decreases. Finally, when humidity rises, a conducting electrolytic layer forms on the surface of the nanotube. The overall resistance of the sensor is reduced since this resistor is used in parallel with the CNT resistor. The Fermi level shift and the depletion layer width grows as a result of charge carrier transfer. Aside from charge carrier transference, two other factors may impact the electrical resistance of the sensor: the chemical interaction of hydrogen (-H⁺ group) with CNT surface oxygen (owing to surface impurities) and the change in nanotube distance [20]. The sensor's sensitivity to humidity, on the other hand, should not interfere with its ability to detect target gases, because surface absorption of the target gas in the presence of dampness would change its resistance value further in comparison to the prior base resistance value. This problem is readily solved by exposing it just to ambient humidity and avoiding other detectable gaseous analytes by utilizing another sensor with identical physical, chemical, and electrical properties as a reference sensor and building the detecting device as an electronic gadget.

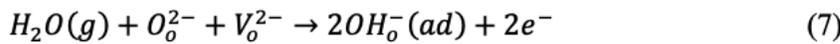
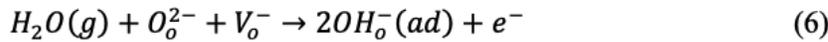
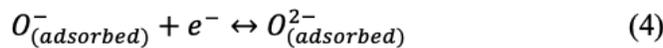
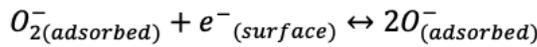
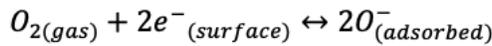
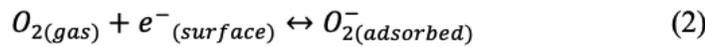
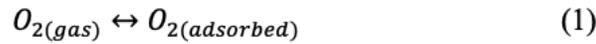
Experiments were also carried out with 100 ppm methane at various temperatures above RT ranging from 30-75°C to evaluate the effect of temperature on sensor responsiveness to methane. The influence of temperature on the sensing device is seen in the inset of Fig. 8. The sensor response becomes virtually constant as the temperature rises to 65°C. The resistance of the sensing film increased as the temperature increases, resulting in an increase in sensor response. The rate of change in resistance per degree increase in temperature, on the other hand, is just 10.2/°C. This implies that the sensors are particularly temperature sensitive. Beyond 65°C (beyond the operable temperature range), there is a rapid rise in resistance and hence sensor response, which is produced by the desorption of ambient humidity from the proximity of the sensor device, as temperature and humidity are inversely related.

3.3.3. Methane sensing mechanism

The electrostatic corona charging approach was used not only to functionalize MWCNTs, but also to generate and attach highly reactive oxygenated sites on f-MWCNTS/Pd nanocomposite thin film [21]. The high temperature created by electrostatic corona agitation ionizes the gas molecules in the film's proximity. As a result, it is thought that during electrostatic corona charging, ambient oxygen, the most

common oxidizing gas, was ionized to native oxygen and adsorbed onto the surfaces of f-MWCNT/Pd nanocomposite. It is widely known that p-type MWCNT-based gas sensors are very common [22,23]. Under ideal environmental conditions, f-MWCNT has a p-type character due to the electron sensitive nature of absorbed moisture or oxygen moieties. When semiconducting p type MWCNTs are exposed to the ambient air, oxygen molecules are adsorbed on their surfaces as per Eq. 1, removing electrons from the MWCNTs' conduction band and generating an electron depletion layer in the surface area, according to Kazemi et al. [24]. As shown in Eq (2) and (3), at low temperatures, O₂ absorbs one electron from the MWCNT surface, but at high temperatures, O₂ absorbs two electrons from the MWCNT surface. Desorbed oxygen molecules occur when adsorbing oxygen molecules interact with other gas molecules. Native oxygen is adsorbed on the surface of MWCNTs, resulting in active oxygenated bond forming sites. MWCNTs will be adsorbed with water molecules from their surroundings, resulting in observable electron donor activity. The described active oxygenation sites are more likely to interact with ambient moisture moieties, resulting in hydroxyl groups as functional or activated sites.

According to Arai et al. [25], based on the processes shown in Eq (5)-(7), non-dissociative and dissociative adsorption schemes may prevail:

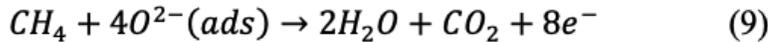
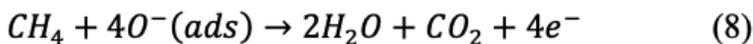


Where V_o^{-} and V_o^{2-} are oxygen vacant sites trapping one or two electrons

The MWCNT-based resistive gas sensor's detection approach is based on changes in the electrical resistance of the MWCNT matrix, which is altered by target gas molecule adsorption-desorption through charge transfer processes. In summary, target gas adsorption on the MWCNT surface can change the electrical resistance by altering the Schottky barrier at the electrode-MWCNT junction, charge transfer between MWCNT and target analytes, and the MWCNT intratubular junction distance [26]. In ambient conditions, MWCNTs obviously act as a p-type semiconductor. The drop in hole concentration generated by electron migration into the valence band of MWCNTs as a result of target analyte assimilation

increases resistance. When electrons are removed from p-type MWCNTs, they enhance hole concentration while lowering resistance. The increased charge agility in MWCNTs generated by the inclusion of scattering sites is also responsible for the change in electrical resistance. Resistance may change if target analytes are adsorbed on the MWCNT-metal interface due to variances in the Schottky barrier. Because a single MWCNT is inadequate to construct a conducting route, the conducting path is often formed by connecting many MWCNTs. If the analytes are adsorbed on the intertube junction, modifying the inter-tubular junctions can also affect MWCNT resistance. The presence of four σ bonds in the methane molecule makes it totally stable and prohibits it from interacting with other molecules via bonding and non-bonding orbitals. High specific area MWNTs are suitable for methane adsorption. However, there is no charge transfer between the inert methane and the MWNTs, resulting in no change in electrical characteristics. As a result, it was observed that pure MWNTs are methane insensitive. The Pd applied to the f-MWNTs in the composite has a significant influence on the methane reactivity of the nanocomposite.

Methane is a reducing gas that works as an electron donor when it interacts with the f-MWCNT/Pd nanocomposite. Methane desorbs chemically adsorbed oxygen ions and physically adsorbed hydroxyl ions from the f-MWCNT/Pd nanocomposite surface during this interaction but enriches it with electrons owing to the oxidation process, as indicated in reaction pathways in Eqs. (8) and (9).



As a result, as shown in Fig. 9, the majority of the charge carriers' holes recombine with the concentration of electrons on the surface of the p-type f-MWCNT/Pd nanocomposite, decreasing the hole concentration and increasing the sensor's resistance depending on the concentration availability of the target gas, methane.

4. Conclusion

Finally, we demonstrated the sensing performance of an electrostatically functionalized and deposited MWCNT/Pd nanocomposite film on a suitable substrate for a highly sensitive, selective, reproducible, and reusable sensing system for detection of traces of the highly toxic and hazardous gaseous analyte methane in air at ambient temperature and pressure conditions. The gas detection device may be reused numerous times simply by blowing away the adsorbed methane species under atmospheric conditions with zero air. It was discovered that the corona assisted electrostatic self-assembly thin film patterning technique for batch fabrication of gas sensors is quick, simple, low-cost, and conforms to sensor fabrication on large areas of the substrate that can be lithographically patterned to produce an array of sensors. This technique has the potential to be employed in lab-on-a-chip applications, wearable sensors, and other small portable electronic device applications.

Declarations

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CRediT authorship contribution statement

Prashant Shukla: Methodology, Investigation, Conceptualization, Visualization, Writing - original draft. **Pooja Saxena:** Validation, Graphics Designing, Writing - review & editing. **Devinder Madhwal:** Prototype development, Writing - review & editing. **Nitin Bhardwaj:** Experimental Investigation, Set Up Establishment. **V.K. Jain:** Supervision, Writing - review & editing.

Declaration of Competing Interest

The Authors declares that there is no conflict of interest. All authors have approved the manuscript and agree with submission to your esteemed journal.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Figures

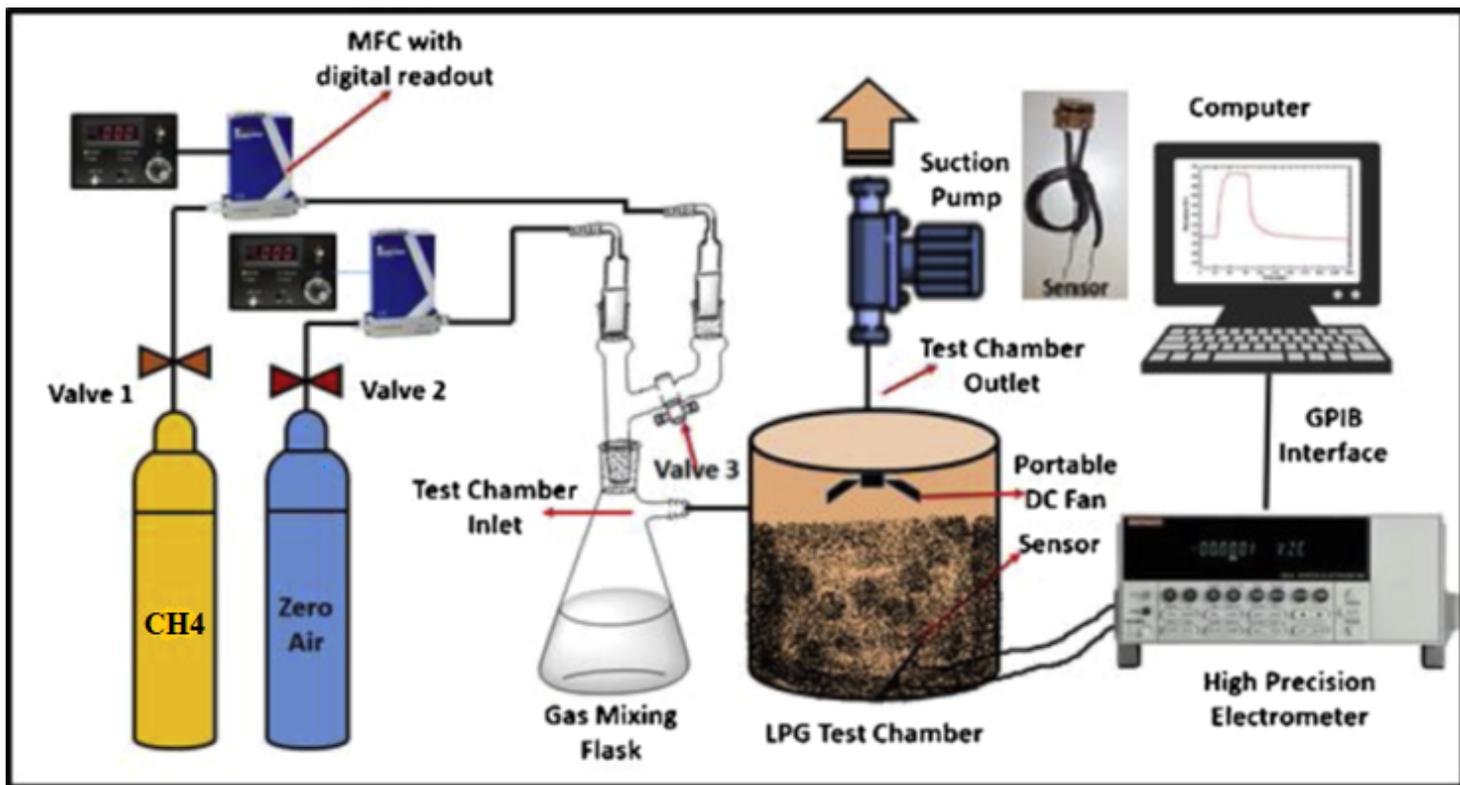


Figure 1

A pictorial representation of the experimental setup for methane sensing.

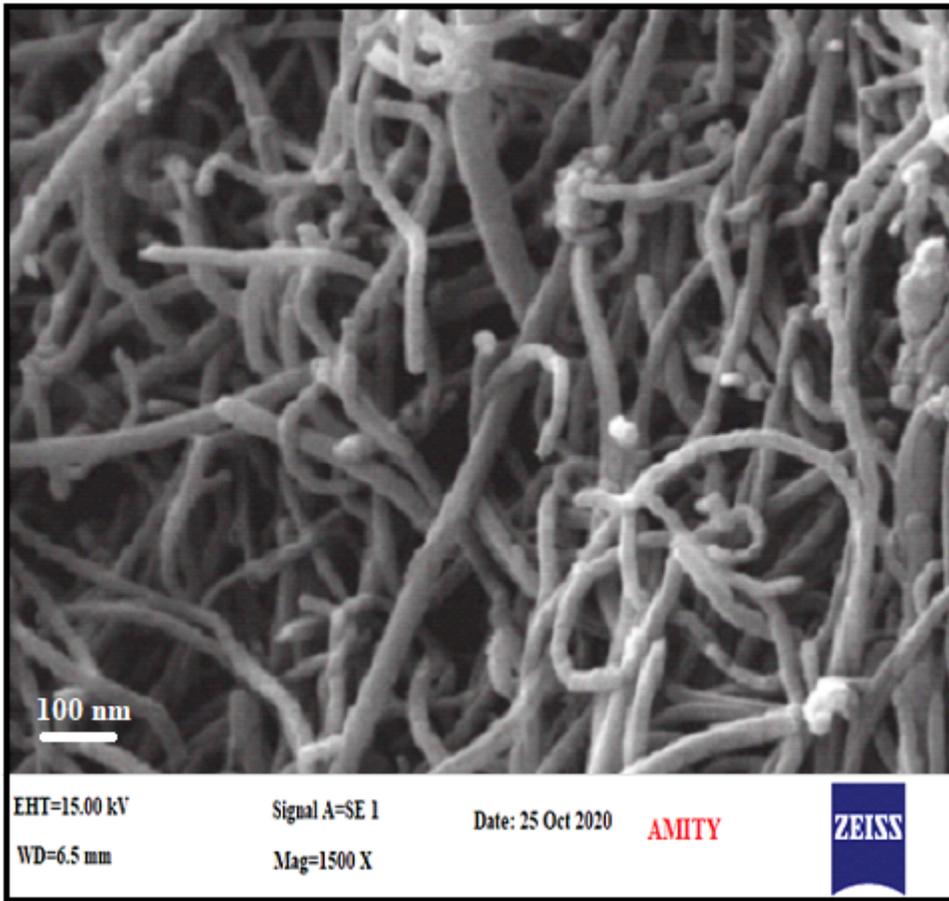


Figure 2

FESEM image of f-MWCNT

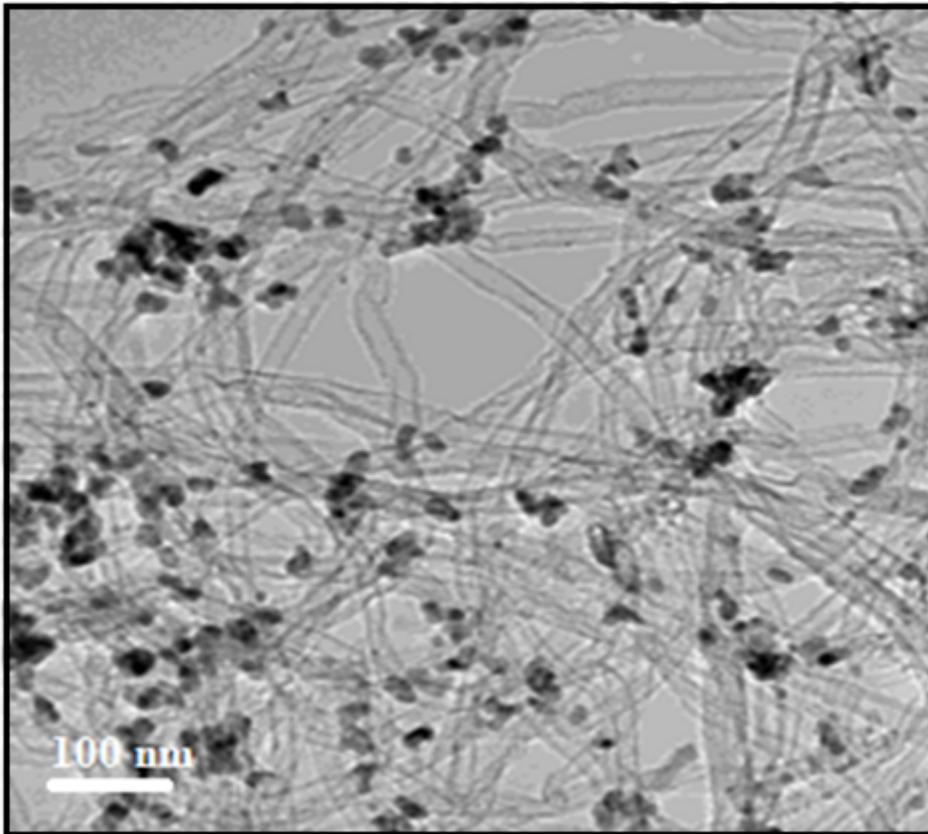


Figure 3

TEM image of f-MWCNT/ Pd nanocomposite

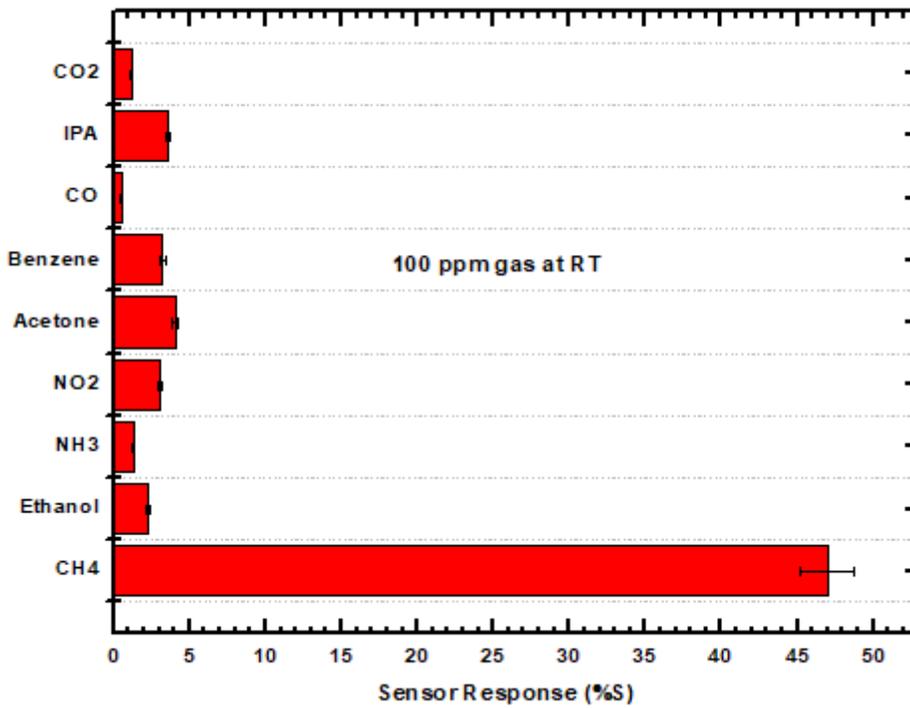


Figure 4

Selectivity and sensor response of f-MWCNT/Pd nanocomposite-based sensor at RT to various gaseous analytes at 100 ppm.

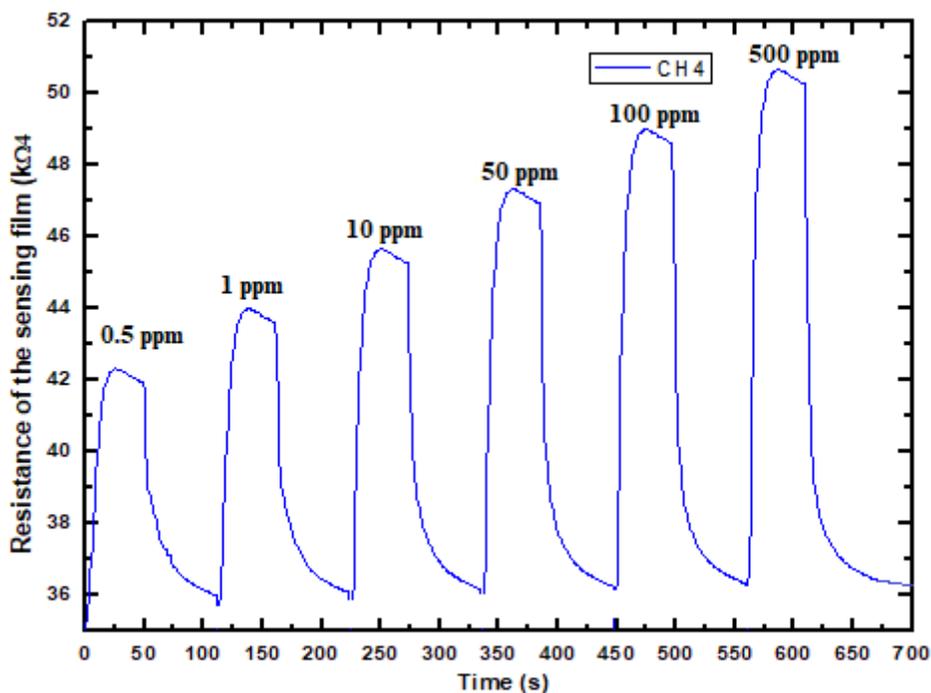


Figure 5

Temporal response of the sensor when exposed to different ppm levels of methane at RT and 1 atm pressure.

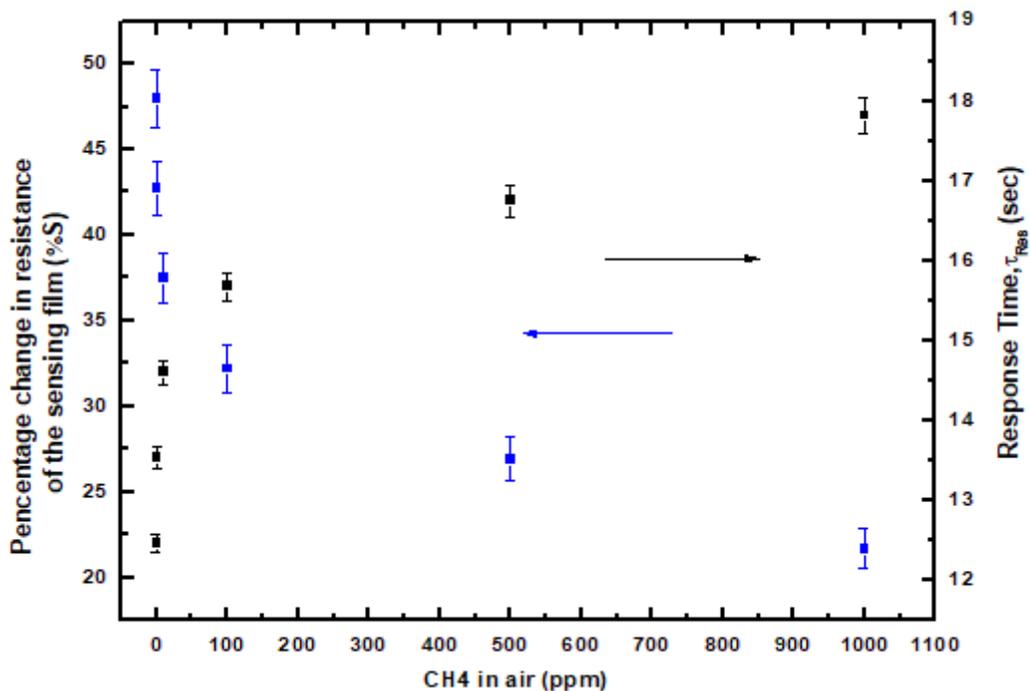


Figure 6

The percentage responsivity (%S) and the sensor response time, τ_{Res} (sec) for methane sensor is plotted against different concentrations varying from 0.5-1000 ppm. The error bars represent $\pm 2\%$ change.

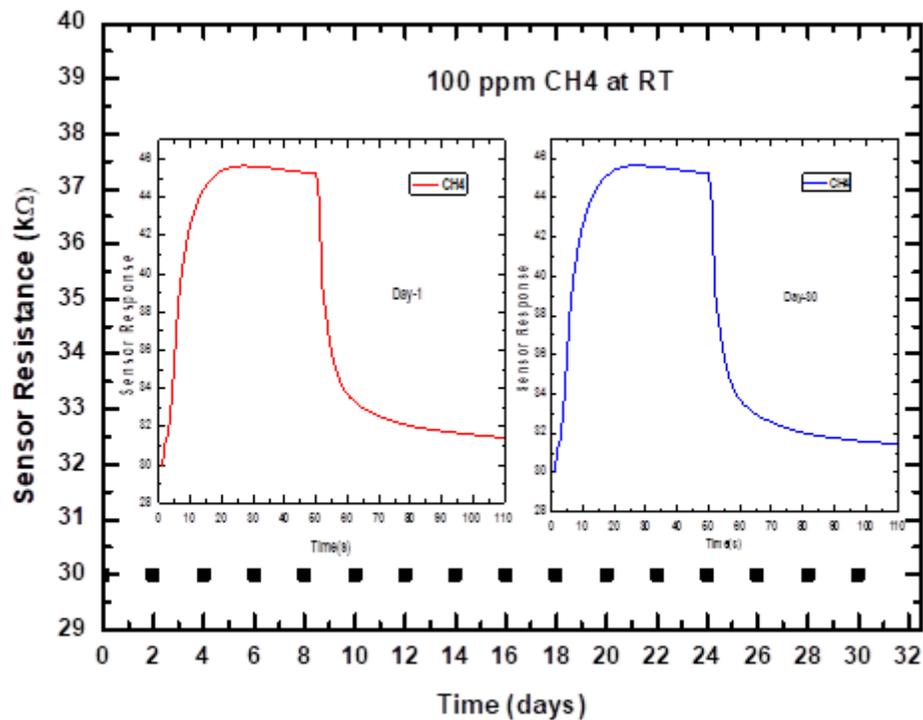


Figure 7

Typical response curves for 100 ppm METHANE at RT performed on the same sensor over 30 days.

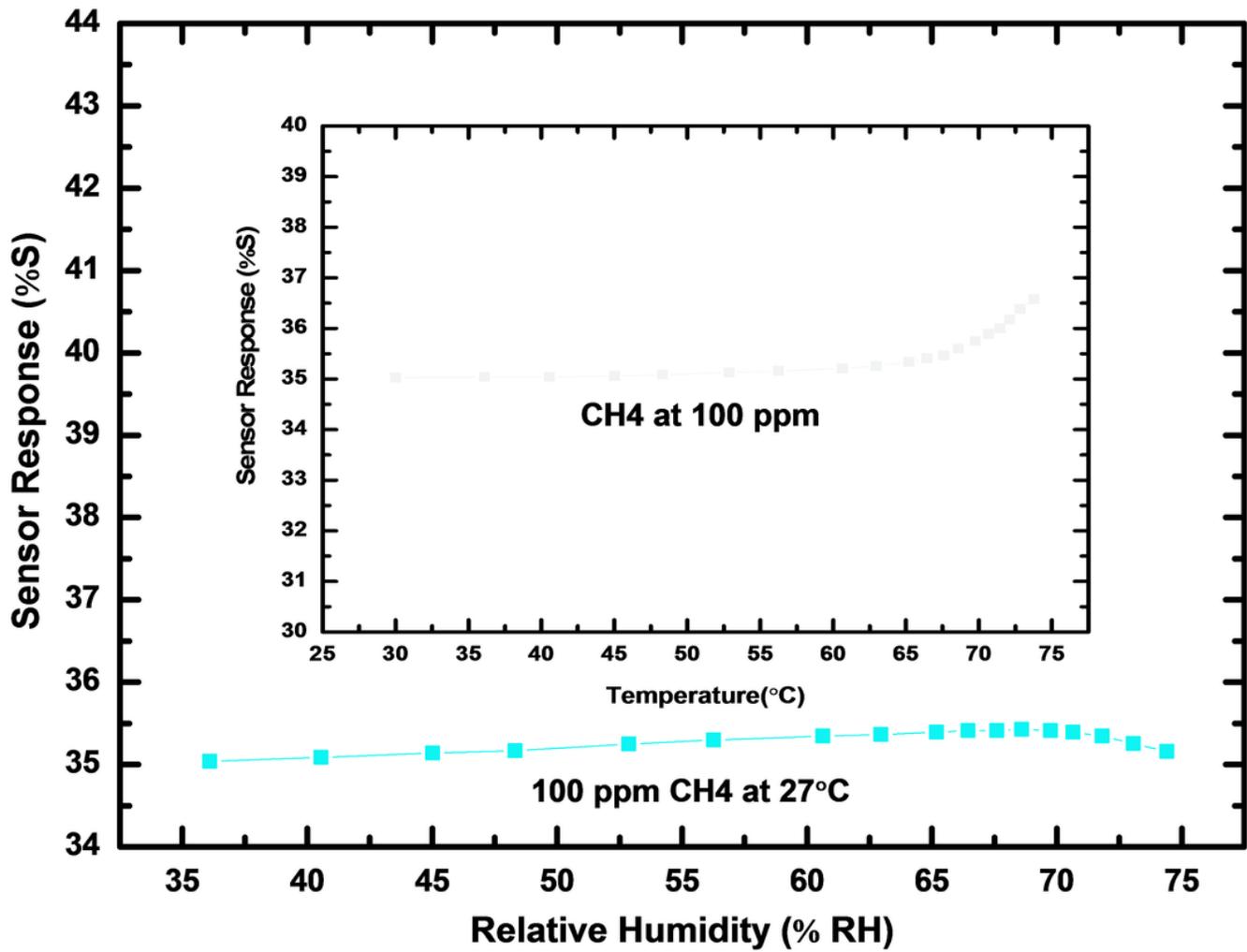


Figure 8

Sensor response (%S): with respect to relative humidity (%RH) and in the inset with respect to temperature (°C).

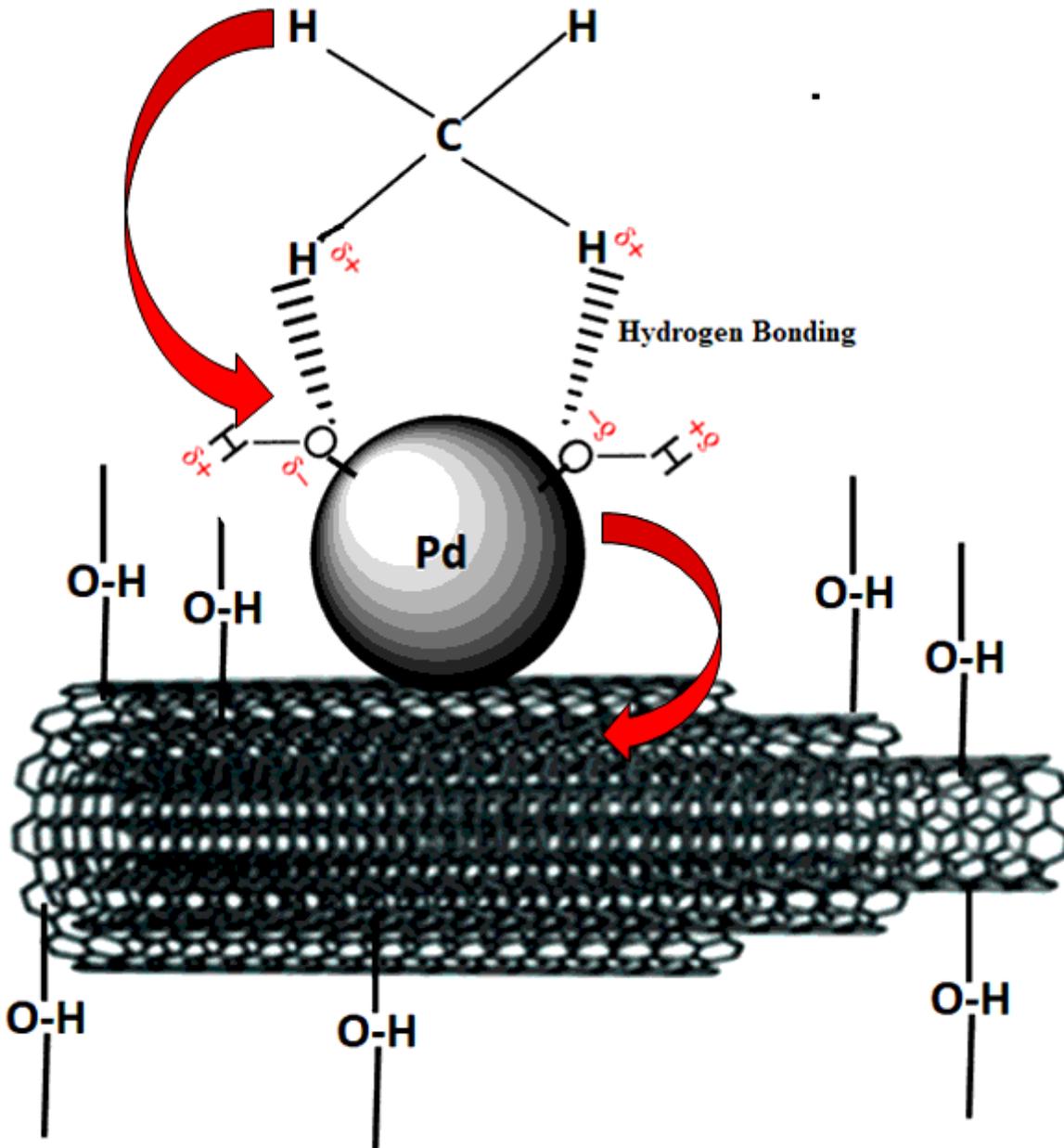


Figure 9

Proposed sensing mechanism for methane detection using f-MWCNT / Pd sensor at RT