

# Nanomaterial-Enabled Chemical Sensors: A Comprehensive Review of Carbon Nanotubes, Metal-Organic Frameworks, and Covalent Organic Frameworks

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## Abstract

**This review researched the latest development of chemical sensors based on the three important nanomaterials, which are Carbon Nanotubes, Metal-Organic Frameworks and Covalent Organic Frameworks. It covered the fundamental sensing mechanisms, methods of synthesis and functionalization strategies in different fields. It also analysed their advantages and limitations to find the research directions which can further improve its performance and practicality. These three nanomaterials chemical sensors bring unprecedented opportunities for the instruction of intelligent and interconnected sensing networks.**

## Keywords

**Carbon Nanotubes, Metal-Organic Frameworks, Covalent Organic Frameworks.**

## 1. Introduction

With the appearance of nanoscale materials, the region of chemical sensors has experienced significant changes. They made the detection of wide range analytes more sensitive and selective. During them, carbon nanotubes (CNTs), metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) have become promising basic materials for the next generation of chemical sensor. They have special structural characteristics, as well as adjustable chemistry properties and excellent electrical properties. These specialties make them useful for different application areas of sensors, such as environmental detection, medical diagnosis, food safety and industrial monitoring.

Chemical sensors which were made by nanomaterials meet the social needs for the real-time monitoring of harmful substances. The daily increasing attention of environmental pollutants, food contaminants and toxic industrial chemicals stimulated deep research for developing high sensitivity, rapid response, portable and cost effectiveness sensors. The traditional methods for sensors could not meet all those needs, therefor it provides sufficient reason for the solution of nanotechnology. By integrating CNT, MOF and COF to the sensing platforms, the detection limits, response time and operational stability have improved significantly, as well as the systems miniaturization and on-site allocation.

This comprehensive review discussed the latest developments of chemical sensors by the three important nanomaterials. The basic sensing mechanics, synthesis and functionalization strategies, as well as the applications in different fields were investigated. The differentiations of their advantages and limits were also analyzed. Their future research orientations for maybe promoting their performance and practicality were also discussed. The integration of those nanomaterials with emerging technologies such as AI, flexible electronics and IoT platforms bring exciting opportunities, especially for creating intelligent and interconnected sensing networks.

## 2. CNTs in chemical sensors

### 2.1. The material of CNTs

CNTs has excellent electronic properties, high surface area and extraordinary mechanical strength, it is widely applied in chemical sensing. When sensors based in CNTs materials interact with the target analyte, the conductivity, the electrochemical activity and optical properties would change. The interaction occurs with physical and chemical absorption, or charge transfer, as well as the notable influence of diameter, chirality and defect density of the nanotubes.

### 2.2. Synthesis and Functionalization

The synthetic methods and functionalization strategies should be concerned carefully when CNTs is applied in practical sensors. CVD is the widely used technology when produce high-quality CNTs with size adjustable and orientation. However, the synthetic approach is improving because of the challenge of batch-to-batch consistency and separation of metallic from semiconducting nanotubes. To improve the sensing performance and selectivity, CNTs is often functionalized with various chemical groups or composite materials. For instance, a recent study demonstrated that  $\text{BiVO}_4$ -MWCNTs composites exhibit strong photochemical oxidation capabilities toward various sugar substitute and sweeteners, while MWCNTs enhance film-forming ability and photoinduced electron transfer process [1]. Similarly, Fe-NCNTs with restricted iron nanoparticles has been developed by the pyrolysis of Fe-MIL-101 and ZIF-8. The obtained materials exhibit excellent electrical conductivity and abundant electrochemical sensing active sites [2].

### 2.3. CNT-Based Sensor Applications

In recent years, the application of CNTs-based sensor has expanded significantly. It covered both electrochemical and optical sensing pattern. In electrochemical sensing, CNTs could be applied as excellent electrode modification materials due to their rapid electron transfer kinetics and large electrochemically active areas. A typical example is the sensor based on Fe-NCNTs, which is used for detecting an environment pollutant with potential health risks 4-aminophenol (4-AP). This sensor achieves a low detection limit of 75nM, a linear range of 0.2-50uM, and high recovery rates (102.2% to 105.9%). These parameters highlight their practical application value. In the field of optical sensing, phenomena brought by the CNT-based platform such as fluorescent quenching and surface-enhanced Raman Scattering is utilized to detect various analytes. Table 1 lists performance characteristics of the three different CNT-based chemical sensors.

Table 1 Performance Characteristics of Selected CNT-Based Chemical Sensors

| Analyte               | Sensor Type          | Detection Limit | Linear Range  |
|-----------------------|----------------------|-----------------|---------------|
| Sweeteners (GLU, ERY) | Photoelectrochemical | Not specified   | 10-240mg/L    |
| 4-Aminophenol         | Electrochemical      | 75 nM           | 0.2-50uM      |
| Basic tastes          | Impedimetric         | Not specified   | Not specified |

The integration of CNTs with other nanomaterials further expands their sensing abilities. For example, CNT-polymer composites have been developed for artificial taste applications. Sensor based on the complex of gel polymer and single walled CNTs could identify the module through resist test and principal component analysis. Therefore, it can distinguish the basic flavors, such as acid, sweet, bitter and salty. This method indicates that CNTs based composites can be designed to imitate biological sensing systems. It opened new pathways to biomimetic sensor design.

### 3. MOFs in chemical sensor

#### 3.1. The material of MOFs

MOFs have become highly versatile materials in chemical sensing application, which is due to their tunable porosity, extremely high surface areas and structural diversity. These crystalline materials which are formed by metal ions or clusters linked through organic ligands can create customized sensing environment for target analytes. It is achieved by the precise engineering at the molecular level. Table 2 lists three different types of MOF-based sensors and their performance characteristics. The sensing mechanisms of MOF-based sensors typically involve interaction of altering their electrical, optical or mass-sensitive properties. The interaction is often achieved through guest-host chemical changes induced by the analyte within the porous structure.

Table 2 Selected MOF-Based Sensors and Their Performance Characteristics

| Analyte      | MOF Material                                                               | Sensing Mechanism             | Detection Limit |
|--------------|----------------------------------------------------------------------------|-------------------------------|-----------------|
| Formaldehyde | Ni-CuCAT on graphene                                                       | Chemi resistive               | 0.5ppm          |
| Aflatoxin B1 | Zn/Co-HHTP                                                                 | Electrochemiluminescence      | 0.31pg/mL       |
| PFASs        | Ce-MOF                                                                     | Mult enzymatic activity array | Not specified   |
| m-Xylene     | MOF-derived Co <sub>3</sub> O <sub>4</sub> /In <sub>2</sub> O <sub>3</sub> | Chemi resistive               | Not specified   |

#### 3.2. Tunable Porosity and Design Strategies

The design flexibility of MOFs is one of their most notable advantages in sensing applications. By carefully selecting metal nodes and organic ligands, researchers can control pore size, shape, and functionality to optimize sensor performance for specific targets. For example, bimetallic MOFs have shown exceptional sensing abilities due to synergistic effects between different metal centers. A notable instance is a conductive bimetallic catechol-based MOF (Ni-CuCAT) grown on laser-patterned graphene. This material exhibits outstanding performance for formaldehyde detection at room temperature with fast response times (1-2 seconds) and a low detection limit of 0.5 ppm [4]. Similarly, a self-amplifying bimetallic conductive MOF with Zn/Co nodes and HHTP ligands has been developed for electrochemiluminescence (ECL) detection. Therein cobalt ions enable catalytic cycles and coreactant acceleration to achieve signal amplification [5].

#### 3.3. MOF-Derived Materials and Sensing Applications

Beyond direct applications, MOFs are also served as precursors for deriving various functional nanomaterials which can enhance the sensing performance. MOFs can be converted into metal oxide semiconductors, carbon composites and hybrid materials by controlled thermal treatment. These materials remain the high porosity morphology of the parent MOF while improving conductivity or catalytic activity. For example, MOF-derived Co<sub>3</sub>O<sub>4</sub>/In<sub>2</sub>O<sub>3</sub> heterostructures with tunable cobalt ratios have been designed for selective detection of xylenes [6]. The 3Co: In sensor exhibits high selectivity for m-xylene at 125°C. It is attributed to an increased Co<sup>3+</sup>/Co<sup>2+</sup> ratio and porous flake morphology, which promote stronger adsorption and activation of oxygen molecules on the sensor surface.

The application of MOF-based sensors has expanded into environmental monitoring, medical diagnosis and food safety. In environmental monitoring, a cerium-based MOF (Ce-MOF) with triple enzyme-mimicking activities (oxidase, laccase, and superoxide dismutase) has been developed for detecting perfluoroalkyl substances (PFASs) [7]. Combining this multienzyme-active sensor array with machine learning algorithms, it can successfully distinguish nine different PFASs with 100% prediction accuracy. It also shows steady performance in real samples including seawater, shrimp, and codfish. In food safety applications, the same Zn/Co bimetallic MOF achieved a record-low detection limit of 0.31 pg/mL for aflatoxin B1 (AFB1). The linear range is 0.001–100 ng/mL, which can provide an effective analytical solution for this toxic food contaminant [5].

## 4. COFs in chemical sensor

### 4.1. The material of COFs

COFs is a relatively new class of porous crystalline materials, which has obtained significant attention in sensing applications. COFs have higher thermal and chemical stability, it is entirely composed of strong covalent bonds formed by light elements (H, B, C, N, O). Therefore, it is different of the MOFs which are characterized by metal-ligand coordination bonds. Their predictable periodic structure combined with tunable pore functions and excellent  $\pi$ -conjugation properties makes COFs particularly suitable for optical and electronic sensing platforms.

### 4.2. Structural Design and Fluorescence Properties

COFs can form precise structure through reversible covalent bonds, therefore, it can carry out atomic-level control by architecture and functionality. This smart design can create a material with customized hole environment and specific interaction sites for target analytes. A promising strategy is using COFs with intramolecular charge transfer (ICT) capabilities for fluorescent sensing. For instance, researchers have developed ICT-induced fluorescent color-changing COFs which contain cationic pyridinium site. So, the sensors which can be highly response to volatile amines can be developed. When exposed to the amine molecules, a significant fluorescence enhancement (fluorescence quantum yield > 13%) and a clearly visible distinct color change will be produced by the deprotonation of the pyridinium site. This sensor exhibits an ultrafast response time of 0.65 seconds to ammonia gas (51.8ppm), which is superior to many other previously reported ammonia sensors with nanostructures.

### 4.3. Composition Tuning and Emerging Applications

The performance of COFs sensor can be finely controlled by strategic component modifications. A noticeable example is deploying COFs with different doping ratios of OMe/OH groups. These groups can obviously change the photochemical behavior through synergistic effect by aggregate-induced emission (AIE), ICT, and excited-state intramolecular proton transfer (ESIPT) [9]. Among these materials, [OMe]<sub>2</sub>-TzDa with an OMe/OH ratio of 2:1 exhibits the strongest fluorescent emission in aqueous solution, as well as the best linearity for pH detection. This optimized COFs sensor is a multimodal sensor for pH, HCl, NH<sub>3</sub> gas, and N<sub>2</sub>H<sub>4</sub> detection, which high-light the universality of precise molecular engineering.

The application of COF-based sensors has expanded to many fields, such as food quality monitoring and environmental analysis. In food spoilage assessment, the previously mentioned fluorescent color-changing COF film has successfully used for monitoring the production of volatile amines. It is achieved by correlating total volatile basic nitrogen (TVB-N) with the sensor's red/green/blue (RGB) output [8]. This method achieves excellent linear correlations for fish ( $R^2 > 0.9987$ ) and shrimp meat ( $R^2 > 0.9917$ ), it enables the monitoring of food freshness visual, AI automation and quantitative. These applications are attributed to the intrinsic

advantages, including high surface area and predictable porosity, as well as the ability to introduce diverse functional groups without compromising crystallinity or stability.

## 5. Comparative Analysis and Future Perspectives

### 5.1. Comparison of three nanomaterials

Every material has its special advantages and limits by comprehensive inspection of the three materials' application in chemical sensor. CNTs perform well in electronics and electrochemical sensing due to its prominent charge transport properties and mechanical robustness. MOFs provide incomparable design diversity and molecular recognition by adjustable pore structure. COFs play extraordinary performance especially fluorescence in optical sensing applications, which combines the advantages of crystallinity and organic components. These complementary advantages are crucial to the choice of selecting appropriate material for special sensing scenario, as well as designing mixed method for multiple material system. Table 3 displays the key characteristics of the three nanomaterial sensors.

Table 3 Comparison of Key Characteristics for Different Nanomaterial Sensors

| Parameter                            | Carbon Nanotubes                                                           | Metal-Organic Frameworks                                                | Covalent Organic Frameworks                                                 |
|--------------------------------------|----------------------------------------------------------------------------|-------------------------------------------------------------------------|-----------------------------------------------------------------------------|
| Primary Sensing Mechanisms           | Electrical conductivity changes, electrochemical activity                  | Host-guest interactions, catalytic activity, structural transformations | Fluorescence changes, colorimetric responses, impedance variations          |
| Key Advantages                       | Excellent electrical conductivity, mechanical strength, fast response      | Extremely high surface area, tunable porosity, diverse functionality    | Pre-designable structures, enhanced chemical stability, strong fluorescence |
| Common Limitations                   | Bundling tendencies, metallic/semiconductor mixture                        | Limited stability in moisture, moderate electrical conductivity         | Complex synthesis, limited structural diversity compared to MOFs            |
| Typical Functionalization Approaches | Covalent sidewall modification, non-covalent wrapping, composite formation | Metal node variation, linker functionalization, core-shell structures   | Pre- and post-synthetic modification, doping, multivariate synthesis        |

### 5.2. Performance Comparison and Integration Strategies

It is found that several key factors became the determined ones in the sensor's performance by comparing the three nanomaterials' practical applications. Different nanomaterials and configurations have different sensitivity and detection limit. Some MOF and COF-based sensors have achieved remarkable detection capabilities of one part per billion or even one part per

trillion for specific analytes. Response time is another key parameter. CNT-based sensors show faster response due to their fast charge transport mechanisms, while MOFs and COFs sensors may need additional time to let the analyte diffuse into its porous structure. Selectivity remains challenge, though MOFs and COFs provide direct path for molecular recognition by cone engineering and functional display.

To overcome individual limitations and create sensors with enhanced functions, it is a promising strategy to integrate different nanomaterials into hybrid structure. For example, combining CNT with MOF can produce a special material which both has CNTs' excellent conductivity and MOFs' selective absorption. Similarly, COF-MOF hybrid material has been explored to create hierarchical pore structure and versatility. To maximize the collaborative potential of the complexed materials, interface interactions and charge transfer process require be carefully optimized.

### 5.3. Current Challenges and Future Directions

Although nanomaterial-based chemistry sensor has achieved promising progress, people still need to face the challenge of practical application. Long-term stability under the operating condition is still a concern, especially the water-sensitivity MOFs and easily oxidized CNTs. Many synthetic methods lack reproducibility, which is required in industrial production. Therefore, manufacturing expandability and batch to batch consistency prevented large-scale commercialization. Furthermore, signal drift and environmental interference still remains challenge to reliable field deployable.

Several future research directions may impact the sensor field. They include developing self-healing materials after degradation or contamination, machine learning algorithms integrated for advanced pattern recognition and drift correction, set up multiplexed sensor arrays which can highly inspect many analytes. Furthermore, the concern of sustainability will promote the research of green synthesis path and degradable sensor platforms to minimize environmental impact. Nanomaterial sensor integrated with wearable technology, IoT platforms and real-time diagnostic system will take exciting opportunity for real-time environment and health monitoring of daily life.

## 6. Conclusion

This review mainly introduced the significant progress and diversity applications of the three nanomaterials CNTs, MOFs and COFs in chemical sensing. Each material provides special advantages for solving the sensing challenges in environmental monitoring, medical care, food safety and industrial application. CNTs can keep advantages in electronic and electrochemical conductive platforms, while MOFs can provide unprecedented opportunities for the molecular identification by adjustable porous structure. COFs have become the promising material for optical sensing by utilizing its strong fluorescence and colorimetric response capabilities.

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