

Advancement of Electrospun Carbon Nanofiber Mats in Sensor Technology for Air Pollutant Detection [†]

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Abstract: The use of electrospun carbon nanofibers (ECNs) has been the focus of considerable interest due to their potential implementation in sensing. These ECNs have unique structural and morphological features such as high surface area-to-volume ratio, cross-linked pore structure, and good conductivity, making them well suited for sensing applications. Electrospinning technology, in which polymer solutions or melts are electrostatically deposited, enables the production of high-performance nanofibers with tailored properties, including fiber diameter, porosity, and composition. This controllability enables the use of ECNs to optimize sensing applications, resulting in improved sensor performance and sensitivity. While carbon nanofiber mats have potential for sensor applications, several challenges remain to improve selectivity, sensitivity, stability and scalability. Sensor technologies play a critical role in the global sharing of environmental data, facilitating collaboration to address transboundary pollution issues and fostering international cooperation to find solutions to common environmental challenges. The use of carbon nanofibers for the detection of air pollutants offers a variety of possibilities for industrial applications in different sectors, ranging from healthcare to materials science. For example, optical, piezoelectric and resistive ECNs sensors effectively monitor particulate matter, while chemoresistive and catalytic ECNs sensors are particularly good at detecting gaseous pollutants. For heavy metals, electrochemical ECNF sensors offer accurate and reliable detection. This brief review provides in-sights into the latest developments and findings in the fabrication, properties and applications of ECNs in the field of sensing. The efficient utilization of these resources holds significant potential for meeting the evolving needs of sensing technologies in various fields, with a particular focus on air pollutant detection.

Keywords: sensors; electrospun nanofiber mats; carbon nanofibers; air pollutant detection



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1. Introduction

Recent advancements in sensing materials are playing a crucial role in enhancing the sensitivity, selectivity, and stability of sensors for industrial applications in environmental monitoring and pollutant detection. These components are of great importance in the enhancement of sensor sensitivity, selectivity and stability, which are essential for accurate environmental monitoring and pollutant detection [1]. Recently, electrospun carbon nanofiber (ECN) mats have attracted considerable attention owing to their exceptional

structural properties, impressive mechanical strength, and remarkable electrical conductivity [2]. These nanomaterials are mainly prepared using electrospinning technology from a variety of bio-based and synthetic polymers or, for example, by adding magnetic particles. The unique combination of properties of ECN mats, including their large surface area, tunable porosity, exceptional electrical conductivity, and mechanical robustness, make them an ideal substrate for a variety of sensing applications [3,4]. In particular, the use of electrospun ECN mats has proven to be a versatile and promising platform for the advancement of sensors in various fields ranging from environmental monitoring to healthcare and beyond [5–7]. These sensors can effectively utilize the advantageous properties of ECN mats to detect and quantify various analytes, including gasses, chemicals, biological molecules and physical parameters [8,9]. Electrospinning involves applying an electric field to a polymer solution or melt, resulting in the formation of ultrafine fibers that can be collected as nonwovens or well-organized arrays. After a carbonization step, these nanofibers transform into a conductive and porous network that serves as an ideal basis for numerous sensor applications. For example, Hou et al. developed a cellulose–nanofiber capacitive humidity sensor with high sensitivity and fast recovery [10]. Caesium–cellulose nanocomposites and their effects on detecting nitrogen gas were investigated by Park et al. and showed promising applications in gas sensing [11]. De Souza et al. investigated carbon nanofibers grown in CaO that could sense themselves in mortar for structural monitoring in building materials [12]. Free-standing, translucent ZnO–cellulose–nanocomposite films with promising unique properties for UV sensing applications were developed by Komatsu et al. [13]. Chemiresistive gas sensors based on chemical vapor deposition (CVD)-grown CNF mats for NO₂ detection at room temperature were investigated by Lapekin et al. [14]. Meenakshi et al. prepared carbon nanofiber (CNF) mats to form CNF/CuWO₄ nanocomposites by a simple hydrothermal method and investigated the composite for electrochemical detection of hazardous organic pollutants such as 4-nitrotoluene (4-NT). The well-defined CNF/CuWO₄ nanocomposite was used as a glassy carbon electrode (GCE) modifier to form a CuWO₄/CNF/GCE for the detection of 4-NT. The electrode showed a remarkable sensitivity of 7.258 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$, a low detection limit of 86.16 nM, and a long linear range of 0.2–100 μM . The electrode was characterized by high selectivity, acceptable stability of about 90% and good reproducibility [15]. Karlapudi et al. combined electrospinning and spray coating processes to fabricate nanofibers with conductive sensing properties. Their electrospun CNF mats exhibited excellent performance characteristics. These included exceptional sensitivity with a gauge factor of about 28.2 over a strain range of 0% to 80%. The CNF mats exhibited high ductility of up to 184%, demonstrating their elasticity under load and remarkable durability [16]. CNF mats have demonstrated remarkable versatility and potential as a platform for advanced sensors, particularly in the context of environmental monitoring. These nanofibers are capable of effectively detecting a wide range of pollutants, including gaseous contaminants such as CO, NO₂, NH₃, and volatile organic compounds such as benzene and toluene. Furthermore, they are capable of identifying heavy metal ions (Pb²⁺, Cd²⁺, Hg²⁺) and organic pollutants such as pesticides, herbicides, and phenolic compounds. Additionally, CNFs can be integrated with piezoelectric or optical systems for monitoring particulate matter, thereby demonstrating their adaptability for air quality assessment applications. In addition, ECNFs can be integrated with piezoelectric or optical systems to monitor particles, enabling versatile applications in air and water quality monitoring. This brief review highlights the use of the properties of CNF mats for the effective detection and quantification of various analytes, such as gasses and chemicals, for the purpose of air pollutant detection.

2. Fabrication Process of Electrospun Carbon Nanofiber Mats

The fabrication of electrospun ECN mats involves a multistep process, and variations in parameters, equipment, and materials are critical to the design of the final ECN mat product [17–20]. The process starts with the selection of a suitable polymer material, which can be natural or synthetic, depending on the desired properties of the ECN mats and the

possible material fusion with, for example, ceramics or metal nanoparticles. Nanofibers can be made from a wide variety of natural and synthetic polymers, although natural polymers are more likely to contribute to sustainability. Both natural polymers, e.g., polysaccharides, lignin, collagen, cellulose, and synthetic polymers, e.g., polyacrylonitrile (PAN), poly(lactic acid) (PLA), acrylonitrile butadiene styrene (ABS), polyurethane (PU), are widely utilized in electrospinning technology. Common synthetic options include polyvinyl alcohol (PVA), poly(ethylene glycol) (PEG), polystyrene (PS), polypropylene (PP), polyethylene terephthalate (PET), and polyamide-6 (PA-6). Among these, PAN and lignin are frequently employed for fabricating carbon nanofiber mats due to their favorable properties for carbonization [21]. The selected polymer is usually dissolved in a compatible solvent such as dimethylformamide (DMF), dimethylacetamide (DMAc), tetrahydrofuran (THF), or dimethylsulfoxide (DMSO). These solvents are known for their good solubility and volatility, which are essential for the electrospinning process [22,23]. The advantage of electrospinning technology is the simplicity of the composition of bio-based or synthetic polymers or a mix of both (see Figure 1a PAN with magnetite particles) and the possibility of adding, for example, magnetic particles (see Figure 1b PAN/gelatin nanofiber mat) in one step.

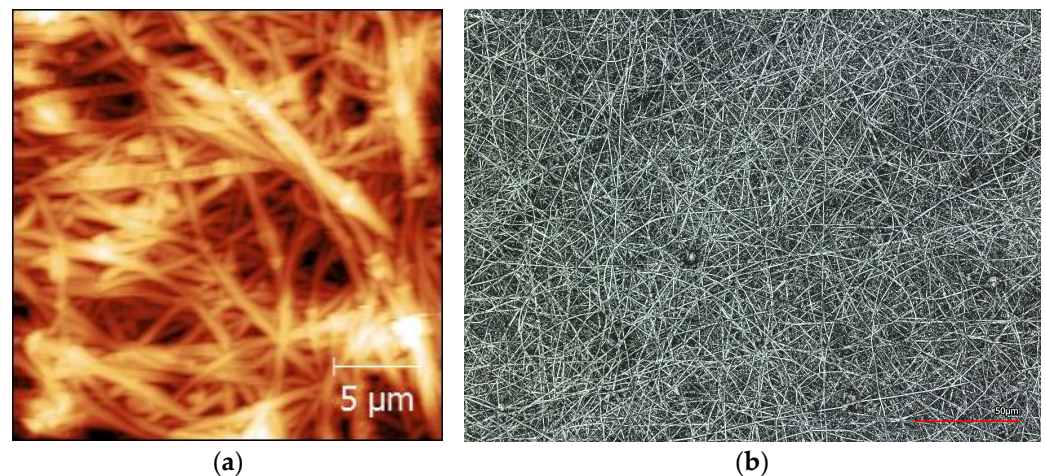


Figure 1. (a) Atomic force microscopy (AFM) image of magnetic electrospun nanofiber mat. The scale bar shows 5 μm ; (b) confocal laser scanning microscope (CLSM) image showing the PAN/gelatin nanofiber mats on a 3D-printed sample. The scale indicates 50 μm .

There is a growing interest in the use of electrospinning for the production of nanofiber mats, with a variety of techniques being employed, including melt, coaxial, multi-jet, and bubble electrospinning. Electrospinning is the most prevalent and uncomplicated technique, capable of generating uninterrupted nanofibers from materials including polymers, composites, ceramics and nanoparticles [19]. The electrospinning process requires a well-calibrated system consisting of a spinneret, a high-voltage supply and a collector. By applying a high voltage to the spinneret, an electric field is generated between the polymer solution and the collector, and a Taylor cone structure is formed. As the electrostatic forces exceed the surface tension of the solution within the Taylor cone, nanofibers are formed and solvent evaporates [24]. There are two main types of electrospinning processes: needle-based and needleless. Needle-based systems can be oriented either vertically or horizontally, whereas needleless systems employ rotating or stationary spinnerets to generate fibers directly from liquid surfaces through Taylor cone formation. The quality of the fibers produced is dependent upon a number of factors, including the properties of the solution, the operating parameters employed, and the environmental conditions in which the process is conducted [25]. These nanofibers are collected on the grounded collector to form nonwoven mats or ordered arrays. Investigation of the surface morphology of electrospun nanofibers can be performed using various techniques such as a scanning

electron microscope (SEM), atomic force microscopic (AFM) or confocal laser scanning microscope (CLSM).

The precise electrospinning process enables the properties of CNF mats to be tailored for specific applications, with careful consideration of process parameters, equipment and materials used [26]. The use of polymers such as polyacrylonitrile (PAN) involves a two-step process: first, a stabilization phase in an oxygen-rich environment to increase thermal resistance, usually by 280 °C [27], and then carbonization at high temperatures (usually above 800 °C) in an inert atmosphere, resulting in the conversion of the polymer into pure CNF mats [28,29].

3. Functionalization and Surface Modification of Carbon Nanofiber Mats

Key principles for sensor operation include selectivity, sensitivity, linearity, response time, and calibration. Factors such as sensor type, transduction mechanism, materials, operating conditions, power requirements, data interface, and packaging must be considered when designing an efficient sensor. Sensor performance evaluation includes assessment of accuracy, precision, resolution, sensitivity, range, response time, stability, noise, and interference. Sensors play an important role in various applications and enable the measurement of different characteristics. Understanding critical design factors and performance characteristics is critical to developing reliable and accurate sensors that drive technical and scientific progress [30–34].

To achieve high selectivity in sensor applications, the surface properties of CNF mats often need to be tailored to interact specifically with target molecules or analytes. This can be achieved by functionalization and surface modification methods [35]. In covalent functionalization, specific functional groups are chemically attached to CNF mats, enabling precise control over their distribution and nature. Non-covalent functionalization methods bind functional molecules or polymers to CNF mats through weak interactions such as stacking, hydrogen bonds, or van der Waals forces and offer reversibility and suitability for specific applications. Some researchers are contributing to progress in the field of functionalization and modification of carbon nanofiber mats. Hung et al. utilized specific surface area measurements and mass loss analysis to investigate the interaction between carbon nanofibers and multilayer carbon nanotubes produced via catalytic pyrolysis of CH₄ with alkalis [36]. CVD enables the controlled deposition of thin films or functionalized layers on CNF mats, which is advantageous for the preparation of metal nanoparticles or metal oxides to improve sensor selectivity [37]. Molecular imprinting creates specific binding sites for target molecules within CNF mats by adding template molecules during fabrication, resulting in high selectivity. Surface activation techniques such as plasma treatment or chemical etching alter the surface chemistry of CNF mats and improve interactions with specific analytes. In self-assembled monolayers (SAMs), functional molecules are self-assembled in a monomolecular layer on CNF mats, which can be tailored to specific analytes by selecting appropriate functional molecules [38–40]. In a study by Górska et al., a nanocomposite for new electrochemical sensors was obtained by combining the electrospinning of precursor nanofibers, high-temperature heat treatment, and catalytic CVD synthesis of carbon nanotubes directly on the surface of nanofibers [41].

4. Sensor Applications in Air Pollutant Detection

CNF mats have garnered widespread recognition for their versatility in sensor applications, capitalizing on their unique structural and electrical attributes. These sensors harness the remarkable properties of CNF mats to detect and quantify a diverse range of factors, including gasses, chemicals, biological elements, pressure, humidity, temperature, and strain [42,43]. Monitoring the presence of hazardous gasses in industrial settings is crucial to ensure worker safety and prevent accidents [43].

Electrospun carbon nanofiber mats serve as effective sensitive materials in gas sensors for the detection of various air pollutants, including VOCs, nitrogen oxides (NO_x), sulfur dioxide (SO₂), and CO. Their large surface area and porous structure provide a rich inter-

face for gas adsorption, thereby enhancing sensor sensitivity. In addition, functionalization of these nanofibers with specific receptor molecules enables selective detection of targeted pollutants. Ding et al. review the use of electrospun nanofibers in gas sensors, highlighting their larger surface area and superior sensitivity compared to flat films [44]. For example, Platonov et al. stress the critical requirement for safety sensors to facilitate hydrogen use under varying oxygen conditions. Their study assesses electrospun ZnO and ZnO/Pd nanofibers for detecting CO, NH₃, and H₂ in diverse oxygen settings. The results indicate that ZnO/Pd nanofibers exhibit remarkable sensitivity to NH₃ and H₂, making them a promising choice for hydrogen detection in low-oxygen environments due to factors like palladium hydride formation, potential barrier adjustment, and alterations in ZnO characteristics [45]. Chen et al. review recent advancements in electrospun gas sensors capable of detecting a variety of gasses. Various nanomaterial shapes and compositions show excellent sensor performance with high sensitivity and stability, low humidity interference, and fast response times [46].

Electrospun carbon nanofiber mats find application in particulate matter (PM) sensors, allowing for the detection and quantification of airborne particulate matter—a vital metric for evaluating air quality. These mats are proficient at trapping fine particulates on their surface, and variations in electrical conductivity can be directly linked to the concentration of PM in the surrounding air. For example, Halicka and Cabaj discussed the development of aptamer and nanocomposite-based sensors for detecting various metal ions such as Hg²⁺, Cd²⁺, Pb²⁺, and As³⁺. These sensors incorporate CNF or nanowhiskers, often enhanced with metal nanoparticles like PtNPs, AuNPs, and Fe-CNFs. Electrochemical techniques like cyclic voltammetry (CV) and anodic stripping voltammetry (ASV) are employed for analysis, resulting in sensors with outstanding sensitivity, low limits of detection (LOD), and proven selectivity and stability during real sample analysis [47].

VOCs significantly impact air quality and indoor pollution. CNF mats offer a valuable solution for VOC detection by functionalizing them with materials that react to specific VOCs, enabling real-time monitoring and early identification of harmful substances. For example, Yin et al. provide a comprehensive review of carbon-based nanomaterials in VOC gas detection, emphasizing sensor construction strategies and applications in environmental monitoring and disease diagnosis, as well as serving as a resource for future research on high-performance VOC gas sensors using carbon materials [48]. Table 1 shows the different types of carbon nanofibers for pollutant detection.

Table 1. The different types of carbon nanofibers for pollutant detection.

CNFs	Pollutant Detection	References
Graphitized Carbon Nanofibers (GCNFs)	Phenol and lead	[49]
Amorphous Carbon Nanofibers (ACNFs)	Heavy metals, organic pollutants	[50]
Hollow Carbon Nanofibers (HCNFs)	Dyes, VOCs	[51]
Doped Carbon Nanofibers (e.g., N-Doped CNFs)	Heavy metals	[52]
Porous Carbon Nanofibers (PCNFs)	Pharmaceuticals, heavy metals	[53]
Electrospun Carbon Nanofibers (ECNFs)	Targeted pollutants	[54]
Activated Carbon Nanofibers (ACNFs)	Organic pollutants	[55]

Carbon nanofiber-based sensors find applications in both environmental monitoring systems, offering real-time air quality data in urban and industrial areas, especially for tracking emissions from various pollution sources, and in wearable devices. When integrated into wearables, electrospun carbon nanofiber mats enable individuals to monitor their personal exposure to air pollutants on the go, particularly valuable for urban and occupational environments where air quality is a critical concern. For example, Hooshmand and colleagues present the addition of multi-walled carbon nanotubes (MWCNTs), which

significantly enhance the performance of ZnO-based chemiresistive sensors in detecting NH_3 compared to bare ZnO sensors. The incorporation of MWCNTs in the porous spaces between ZnO nanoparticles increases the surface area for gas adsorption, resulting in improved gas detection capabilities. The sensor exhibited high and stable selectivity and sensitivity to NH_3 , even in the presence of CH_4 and CO , at low NH_3 concentrations (10 and 20 ppm). The sensor's key parameters include a response of 1.022, a response time of 13.687 s, and a recovery time of 107.109 s, as depicted in Figure 2, which illustrates the sensor architecture, sensing mechanism, and experimental setup [56].

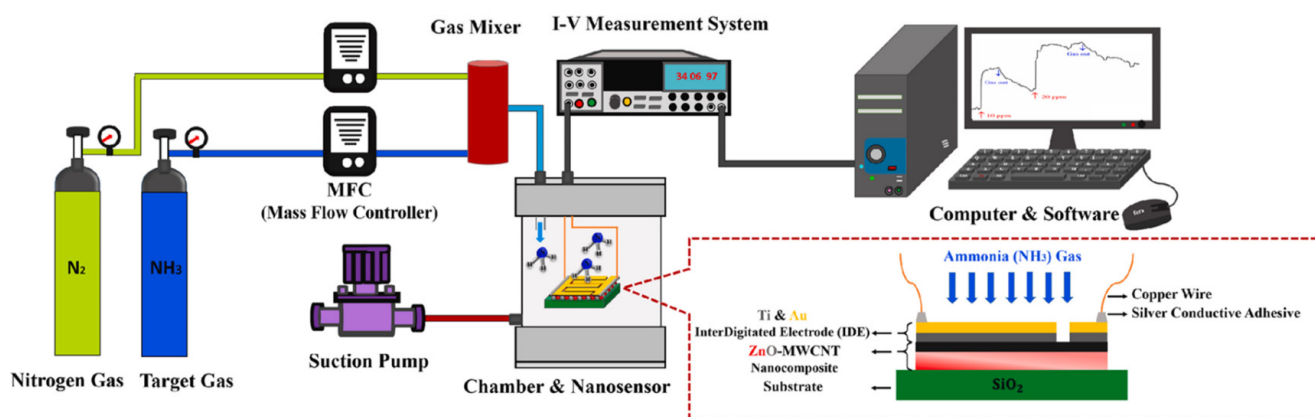


Figure 2. Schematic of experimental setup for the fabrication of ZnO-MWCNT nanocomposite sensor and its ammonia gas sensing properties at room temperature. Reprinted from [56], with permission from Elsevier.

5. Conclusions, Challenges and Future Research Perspectives

This review emphasizes the considerable potential of ECNF mats in sensor technology, particularly for the detection of air pollutants such as carbon monoxide (CO), nitrogen dioxide (NO_2), ammonia (NH_3), and volatile organic compounds (VOCs). Nevertheless, several challenges must be addressed in order to optimize their use, including improvements in selectivity, sensitivity, stability and scalability. For instance, ECNF sensors utilized for CO detection in urban settings may exhibit cross-sensitivity to other gasses, such as NO_2 or VOCs, resulting in erroneous readings. To address this issue, functionalization techniques, such as doping the ECNFs with metal oxides (e.g., tin oxide), can enhance selectivity, thereby increasing the sensor's sensitivity to CO while reducing interference from other pollutants [57].

Another crucial consideration is the biocompatibility of the sensors, which is especially pertinent in the context of wearable technology. To illustrate this, ECNF-based sensors incorporated into clothing or health monitoring devices may be in contact with the skin for extended periods. Moreover, the integration of ECNF sensors with smart devices via machine learning can facilitate real-time data analysis and prediction. For instance, machine learning algorithms can analyze patterns from ECNF sensors monitoring indoor air quality, thereby enabling automatic adjustment of ventilation systems to optimize air quality and reduce the risk of respiratory problems. Furthermore, energy efficiency and flexibility are also pivotal considerations for the prospective evolution of ECNF sensors. Flexible, lightweight ECNF-based sensors can be used in portable devices, such as handheld air pollution detectors or personal wearable air quality monitors [58]. Standardizing test protocols, fostering interdisciplinary collaboration, and clarifying legal and safety issues are essential for progress in this area. Applications span across various sectors, from healthcare to materials science, providing a wide range of opportunities for the use of ECNF mats in sensor technology for the purpose of detecting air pollutants. Electrospun carbon nanofiber mats show substantial potential in the field of air pollutant detection sensor technology as valuable assets in the quest to oversee and address air pollution concerns for the betterment of both the environment and public health.

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