

RESEARCH ARTICLE

High–Sensitive Chemiresistive Sensors Based on a SWCNT/Fe(II) Phthalocyanine Hybrid Nanocomposite for Environmental Carbon Monoxide Monitoring

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ABSTRACT: In response to the escalating global concern over air pollution, the development of reliable and efficient sensors for real-time environmental monitoring has become imperative. This work presents the design and fabrication of a high-performance chemiresistive gas sensor utilizing a hybrid nanocomposite of single-walled carbon nanotubes (SWCNTs) non-covalently functionalized with Iron(II) phthalocyanine (Fe(II)Pc). SWCNTs serve as the conductive framework, while Fe(II)Pc acts as the active sensing layer, leveraging strong π – π interactions to preserve the electronic properties of the nanotubes. The sensors were fabricated via AC dielectrophoretic alignment of SWCNTs across gold microelectrodes, followed by functionalization with Fe(II)Pc. Comprehensive structural characterization using field emission scanning electron microscopy (FESEM) confirmed uniform integration of the hybrid material within the electrode gap. Electrical characterization through current–voltage (I–V) measurements indicated enhanced conductivity and the formation of a charge-transfer complex upon functionalization. The sensing performance was evaluated through exposure to carbon monoxide (CO) at concentrations ranging from 50 to 300 ppm. The devices exhibited a highly sensitive, selective, and reversible chemiresistive response, with detection capabilities extending below the permissible exposure limit (PEL) of 50 ppm. The sensors also demonstrated excellent linearity, reproducibility, and long-term stability over 90 days. These results underscore the potential of SWCNT/Fe(II)Pc hybrid sensors as robust, miniaturizable platforms for real-time atmospheric monitoring of hazardous pollutants.

Keywords: Single-walled carbon nanotubes, Iron(II) phthalocyanine, Chemiresistive sensor, Carbon monoxide detection, Hybrid nanocomposite, Environmental monitoring

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1. INTRODUCTION

Environmental pollution, characterized by the pervasive

introduction of deleterious chemical and biological agents into the atmosphere, represents one of the most pressing challenges of the modern era. This contamination stems from a complex interplay of anthropogenic activities and natural processes. Human-driven sources, including the combustion of coal and fossil fuels, extensive application of agrochemicals, and emissions from industrial operations, continuously discharge vast quantities of pollutants [1]. Concurrently, natural phenomena such as biological respiration and the decomposition of organic matter contribute additional gaseous compounds to the environmental matrix. The relentless accumulation of these

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species, encompassing carbon oxides (CO, CO₂), nitrogen oxides (NO_x), sulfur oxides (SO_x), volatile organic compounds (VOCs), and particulate matter, poses a severe and escalating threat to global ecosystems, biodiversity, and human health, with adverse effects manifesting across all living organisms upon exposure to elevated concentrations [1].

Among this array of pollutants, carbon monoxide (CO) is of particular concern due to its acute toxicity and insidious nature. As a colorless, odorless, and tasteless gas, CO poses a significant stealth hazard. Its primary mechanism of toxicity, as outlined by Occupational Safety and Health Administration (OSHA) guidelines, involves a high-affinity binding to hemoglobin, displacing oxygen and leading to tissue hypoxia and potential fatality [2]. The toxicological profile of CO has been rigorously investigated over decades, with research elucidating its detrimental impacts during critical physiological stages such as pregnancy and neonatal development, its role in impairing cardiovascular function, and its induction of mitochondrial dysfunction through mechanisms that involve the scavenging of crucial cellular signaling molecules [3-5]. These comprehensive studies underscore the imperative to maintain ambient CO levels as low as reasonably achievable. Given that complete avoidance of CO exposure is impractical in industrialized societies, the implementation of robust, continuous monitoring systems becomes not merely beneficial but essential. The real-time detection of CO is a critical prerequisite for enacting timely public health interventions and safety protocols in settings ranging from industrial workplaces to urban environments.

Consequently, significant research endeavors have been directed toward developing sensitive and reliable CO sensors. Various strategies have been explored, including the development of palladacycle-based fluorescence turn-on probes for sensitive detection [6], the design of chromo-fluorogenic probes for visual or optical signaling [7], and the utilization of nanomaterials like reduced graphene oxide (rGO) for room-temperature sensing [8]. While these approaches have advanced the field, they often entail intrinsic limitations that hinder widespread, practical deployment. Such limitations include complex and costly fabrication procedures, operational complexities that require specialized user training, and bulkier form factors that impede integration into portable or distributed monitoring networks. Therefore, a clear and persistent need exists for the creation of a sensing platform that harmonizes high efficiency, selectivity, and sensitivity with straightforward fabrication, user-friendly operation, and inherent miniaturization potential. Addressing this multifaceted requirement hinges critically on the judicious selection of both the sensing modality and the active materials employed in the sensor's design.

In this context, chemiresistive sensors have emerged as a highly attractive paradigm due to their fundamental operational simplicity, low power demands, and excellent compatibility with miniaturization and electronic readout systems. Their working principle relies on monitoring changes in the electrical resistance of a sensing material upon

interaction with a target analyte. This modality becomes particularly powerful when paired with nanoscale materials, such as one-dimensional (1D) or zero-dimensional (0D) nanostructures, which offer high surface-to-volume ratios and pronounced quantum confinement effects, enabling profound electrical responses to surface adsorption events. Single-walled carbon nanotubes (SWCNTs) stand out as one of the most promising materials for such applications. Their exceptional chemical stability, coupled with superior mechanical and thermal properties, allows them to function reliably under diverse and harsh environmental conditions [9]. Their inherent nanoscale dimensions and high aspect ratio facilitate device miniaturization and provide a vast surface area for analyte interaction. Furthermore, the unique electronic structure of SWCNTs, characterized by strong quantum confinement along their 1D axis, renders their charge carrier density exquisitely sensitive to local chemical perturbations, making them among the most potent nanostructured transducing elements available [10].

However, pristine SWCNTs are not without drawbacks as standalone sensing materials. Their pristine graphitic sidewalls, while chemically robust, exhibit limited selectivity and can lead to strong, often irreversible physisorption of certain analyte molecules. This results in poor sensor recovery, slow response dynamics, and a lack of variety in specific transduction mechanisms for different gases, ultimately compromising reproducibility and long-term stability [11, 12]. To overcome these limitations, a powerful strategy involves the supramolecular functionalization of the SWCNT sidewalls. Non-covalent functionalization, in particular, is highly advantageous as it decorates the nanotube surface with active recognition sites while preserving the pristine sp² carbon lattice and its desirable electronic properties. This approach effectively tailors the chemical interface of the SWCNT for specific interactions. Researchers have demonstrated that non-covalently functionalized SWCNTs can achieve highly efficient and selective real-time sensing for various analytes [13, 14]. A wide range of materials can serve as functionalizing agents via this route, including macrocyclic compounds, metallic or metal oxide nanoparticles, and conducting polymers, each imparting distinct chemical affinities [15-17].

Within the family of macrocyclic compounds, metallophthalocyanines (MPcs) have been profusely utilized in chemical sensing due to their rich redox chemistry, structural versatility, and ability to coordinate with a wide range of analytes [18, 19]. Phthalocyanines are synthetic, planar macrocycles analogous to porphyrins, featuring an 18- π electron aromatic system. Their structure can be readily modified through peripheral substitution or by incorporating a central metal ion, such as iron(II), to form complexes like Iron(II) phthalocyanine (Fe(II)Pc). These modifications allow fine-tuning of their electronic and chemical sensing properties. Traditionally, much of the gas sensing research involving phthalocyanines has employed techniques like quartz crystal microbalance (QCM), relying on mass changes, or has involved their deposition as thin films for other transduction methods [19, 20]. The novelty of the present

work lies in the strategic integration of these two advanced material classes to create a synergistic hybrid sensing platform. We report the fabrication of a chemiresistive sensor based on SWCNTs non-covalently functionalized with Fe(II)Pc. This design leverages the high conductivity and nanoscale transduction capability of SWCNTs with the specific, active recognition sites provided by the Fe(II)Pc macrocycles. The non-covalent attachment via π - π stacking ensures optimal electronic communication between the components. This hybrid approach addresses the limitations of prior technologies by enabling room-temperature operation, simplifying fabrication through techniques like AC dielectrophoretic alignment and drop-casting, and enhancing both sensitivity and selectivity through molecular design. Herein, SWCNTs were precisely aligned between microfabricated gold electrodes and subsequently functionalized with Fe(II)Pc. The fabricated chemiresistors were then systematically exposed to varying concentrations of carbon monoxide to evaluate their electrical response and sensing performance.

2. EXPERIMENTAL DETAILS

2.1. Sensor Substrate Fabrication

The foundational platform for the chemiresistive sensors was a p-doped silicon wafer. This substrate was selected for its excellent semiconductor properties, mechanical rigidity, and compatibility with standard microfabrication processes. The wafer featured a thermally grown silicon dioxide (SiO₂) layer with a thickness of 100 nm, which served as an insulating barrier to prevent electrical leakage between the subsequent metallic patterns and the conductive silicon base, which itself was 525 μ m thick. To create robust and well-adhered microelectrodes, a bilayer metal structure was deposited onto the Si/SiO₂ surface. Initially, a 20 nm thick chromium (Cr) adhesion layer was deposited using electron-beam (e-beam) evaporation, a technique chosen for its precision in achieving thin, uniform films. Following this, a 180 nm thick layer of gold (Au) was deposited via thermal evaporation [21]. The desired interdigitated electrode pattern was then defined on this metal bilayer using standard photolithographic techniques. This process yielded pairs of opposing Au microelectrodes, each 200 μ m in width, separated by a critical gap of approximately 3 μ m. This microscale gap is the active region where the sensing material is later integrated. Prior to functionalization, all fabricated substrates underwent a rigorous cleaning procedure involving sequential sonication in acetone and isopropanol to remove organic contaminants and ensure a pristine surface for nanomaterial deposition [22].

2.2. Materials and Chemical Preparation

The primary nanomaterials used in this study were carboxylated single-walled carbon nanotubes (SWCNTs-

COOH), procured from Nanoshel LLC. The functional -COOH groups introduced during synthesis enhance dispersibility in polar solvents. The active sensing moiety, Iron(II) phthalocyanine (Fe(II)Pc, 99% purity), was obtained from Sigma-Aldrich. All chemical preparations utilized high-purity N,N-Dimethylformamide (N,N-DMF, GC grade, Rankem Ltd.) as the solvent due to its effectiveness in dispersing both carbon nanotubes and phthalocyanine compounds [22]. A stable suspension of SWCNTs was prepared by dispersing approximately 0.61 mg of SWCNTs-COOH in 20 mL of N,N-DMF. This mixture was subjected to prolonged sonication for 90 minutes in a VWR 100C ultrasonic bath to exfoliate nanotube bundles and achieve a homogeneous dispersion. To remove any large, unexfoliated aggregates or residual catalyst particles, the sonicated suspension was subsequently centrifuged at 15,000 rpm for 90 minutes using a Remi R-24 centrifuge, with only the supernatant being retained for use. Separately, a 0.1 mM solution of Iron(II) phthalocyanine was prepared in N,N-DMF by magnetic stirring for 60 minutes at ambient temperature to ensure complete dissolution.

2.3. Sensor Fabrication and Functionalization

The integration of the sensing material across the microelectrode gap was accomplished using an AC dielectrophoretic (DEP) alignment technique. This method was selected for its ability to precisely position and align individual nanotubes or small bundles between electrodes, forming conductive bridges. A minute droplet (~0.4 μ L) of the prepared SWCNT suspension was carefully dispensed onto the electrode gap. An alternating current (AC) signal with a peak-to-peak voltage (V_{p-p}) of 3 V and a frequency of 4 MHz was then applied across the electrodes. The resulting non-uniform electric field induces a dipole in the polarizable nanotubes, causing them to migrate toward the region of highest field strength, the electrode edges, and align across the gap. The process was monitored in real-time, and the device resistance was measured after a 10-minute stabilization period to optimize the alignment duration and ensure the formation of a stable conductive network. Following alignment, the substrate was gently rinsed with nanopure water to remove excess solvent and loosely bound nanotubes, followed by drying under a stream of nitrogen gas. To improve electrical contacts and remove residual solvent from the nanotube network, the devices were annealed at 300°C for one hour under a reducing atmosphere (5% H₂ in 95% N₂) [22].

Subsequent functionalization involved decorating the aligned SWCNT network with Fe(II)Pc molecules via non-covalent π - π stacking interactions. A 0.6 μ L droplet of the 0.1 mM Fe(II)Pc solution was drop-cast directly onto the SWCNT bridge and allowed to incubate for 60 minutes at room temperature, facilitating molecular adsorption. The device was then rinsed again with nanopure water to physisorb excess phthalocyanine and annealed at a milder temperature of 100°C under a pure nitrogen atmosphere for

60 minutes. This step promotes a more stable interaction between the Fe(II)Pc and the SWCNT sidewalls while ensuring complete solvent evaporation. All fabrication and subsequent measurements were conducted under controlled ambient conditions ($25 \pm 1^\circ\text{C}$, 35–40% relative humidity) unless otherwise specified.

2.4. Structural, Electrical, and Gas Sensing Characterization

Comprehensive characterization was performed to validate the sensor fabrication and evaluate its performance. The surface morphology and successful integration of the SWCNT/Fe(II)Pc hybrid material within the electrode gap were confirmed using Field Emission Scanning Electron Microscopy (FESEM) on a Hitachi S-4800 system. Electrical characterization was paramount for a chemiresistive device. The current-voltage (I-V) characteristics were measured at each fabrication stage using a CHI 660C electrochemical workstation in linear sweep voltammetry mode, providing insight into the conductivity and the nature of the contacts.

The gas sensing performance was evaluated using a custom-built, computer-controlled dynamic gas mixing and testing system. Fabricated sensors were wire-bonded to a test fixture using a 7476D West Bond wedge bonder to ensure reliable electrical connections. The sensor was then housed in a sealed stainless-steel test chamber with a volume of 8 cm³. Mass flow controllers (MFCs) were used to precisely blend certified carbon monoxide (CO) gas with dry, purified synthetic air to generate specific concentrations (e.g., 50, 100, 150, 200, 250, 300 ppm). The total gas flow rate through the chamber was maintained constant at 200 standard cubic centimeters per minute (sccm) to ensure consistent gas exchange and minimize environmental fluctuations. A constant DC bias of -1.5 V was applied across the sensor electrodes using a Keithley 2400 SourceMeter Unit (SMU). This instrument simultaneously applied the voltage and recorded the resulting current with high precision, allowing the real-time calculation of resistance. The sensing protocol began by flowing dry air to establish a stable baseline resistance (R_{air}). The gas stream was then switched to the desired CO/air mixture for a fixed exposure interval, followed by a recovery phase with dry air. The sensor response was defined as the relative change in resistance. To ensure statistical significance and account for device-to-device variation, the entire experimental procedure was repeated for five independently fabricated sensor devices.

3. RESULTS AND DISCUSSION

3.1. Structural and Morphological Analysis via Field Emission Scanning Electron Microscopy

The successful integration and hybrid formation of the sensing material was first verified through structural characterization. Figure 1 presents a representative field

emission scanning electron microscopy (FESEM) image of the fabricated device, capturing the critical region between the two gold microelectrodes. The micrograph clearly shows a network of fibrous structures bridging the electrode gap, confirming the effective deposition and alignment of single-walled carbon nanotubes (SWCNTs). The utilization of the AC dielectrophoretic (DEP) alignment technique proved highly effective, as evidenced by the directed orientation of nanotubes preferentially spanning the shortest path between electrodes, rather than forming a random mesh. This controlled alignment is crucial for creating reproducible and efficient conductive pathways. A critical observation from Figure 1 is the apparent diameter of the deposited structures, measured to be approximately 45 nm. This dimension is significantly larger than the typical diameter of pristine SWCNTs (which are often 1–2 nm), strongly indicating that the nanotubes are coated or decorated with another material. This increase in diameter provides direct visual evidence for the successful non-covalent functionalization of the SWCNT sidewalls with Iron(II) phthalocyanine (Fe(II)Pc) molecules. The Fe(II)Pc molecules, through π - π stacking interactions, have adsorbed onto the nanotube surfaces, forming a conformal layer. This morphological analysis confirms that the adopted fabrication protocol, sequential DEP alignment of SWCNTs followed by solution-phase functionalization, is a robust method for creating a well-defined, hybrid nanomaterial-based sensing interface on a microfabricated platform.



Fig. 1. FESEM image of aligned SWCNTs bridged across Au electrodes. The increased diameter (~45 nm) indicates non-covalent functionalization with Fe(II)Pc.

3.2. Electronic Properties and Charge Transfer Complex Formation

The electronic interaction between the SWCNT backbone and the Fe(II)Pc functional layer was probed through current-voltage (I-V) measurements, the results of which are

displayed in Figure 2. The I-V characteristics for both the pristine SWCNT network and the SWCNT/Fe(II)Pc hybrid were recorded. A fundamental and revealing trend was observed: following functionalization with Fe(II)Pc, the device exhibited a marked decrease in resistance, corresponding to an increase in conductivity. This observation is pivotal to understanding the hybrid's electronic structure. The pristine SWCNTs used in this study are known to exhibit p-type semiconductor behavior in ambient conditions, primarily due to oxygen adsorption. The introduction of Fe(II)Pc, a macrocyclic compound with a rich π -electron system and a redox-active iron center, facilitates a charge transfer interaction at the interface. The Fe(II)Pc molecule likely acts as an electron donor to the p-type SWCNTs. This electron donation partially compensates for the hole carriers (majority charge carriers) in the SWCNTs, leading to a modulation of the Fermi level and a resultant decrease in electrical resistance. The linear and symmetric nature of the I-V curves both before and after functionalization indicates good ohmic contact formation at the Au-SWCNT junctions. The pronounced change in slope (inverse of resistance) directly evidences the formation of a charge-transfer complex between the phthalocyanine macrocycle and the nanotube, as supported by similar phenomena reported in literature for related porphyrin-nanotube systems [23]. This enhanced electronic coupling is not merely a side effect but a foundational aspect of the sensing mechanism, as it creates a system where the electronic density of the SWCNT is sensitively tuned by the state of the Fe(II)Pc adsorbates.

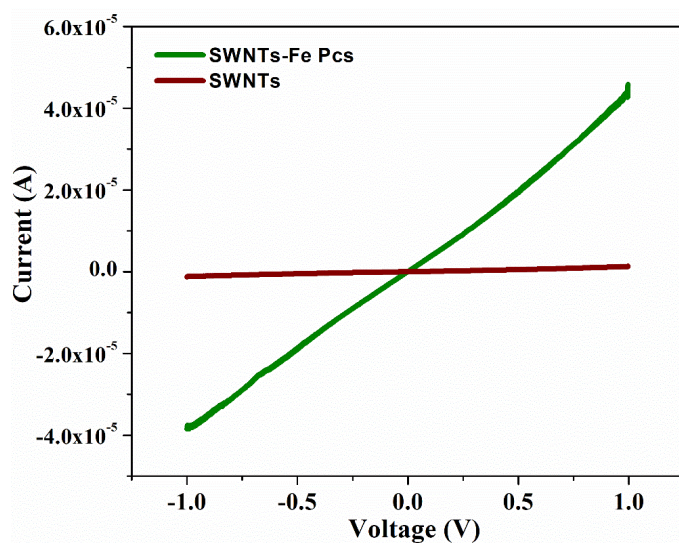


Fig. 2. I-V characteristics of pristine (black) and Fe(II)Pc-functionalized (red) SWCNTs. Enhanced conductivity after functionalization confirms charge-transfer complex formation.

3.3. Chemiresistive Response to Carbon Monoxide

The core functionality of the fabricated hybrid as a carbon

monoxide sensor was evaluated under dynamic gas flow conditions at room temperature ($25 \pm 1^\circ\text{C}$). The sensor's response, defined as the relative change in resistance ($\Delta R/R_0$), was recorded upon exposure to varying concentrations of CO, ranging from 50 ppm to 300 ppm. The summary of this data is presented in the histogram in Figure 3, which clearly illustrates a concentration-dependent response. As the CO concentration increased, a systematic and reproducible increase in the normalized resistance was observed. This positive response (increasing resistance for a p-type semiconductor) is indicative of an electron-donating interaction between the target gas and the sensing material. When CO molecules adsorb onto the active Fe(II)Pc sites, they can donate electron density into the hybrid system. For a p-type SWCNT backbone, where hole conduction is dominant, the injection of electrons leads to a recombination event that reduces the hole carrier density. A reduction in the number of majority charge carriers manifests as an increase in the measured electrical resistance. This mechanism aligns with previous studies on electron-donating analytes interacting with p-type nanostructured materials [24]. Significantly, the sensor generated a measurable and consistent response at 50 ppm, which is the permissible exposure limit (PEL) for an 8-hour time-weighted average as per OSHA guidelines. This demonstrates the device's immediate relevance for health and safety monitoring. Furthermore, the trend suggests that with further optimization of fabrication parameters, such as SWCNT network density or Fe(II)Pc loading, the limit of detection could be pushed significantly below this threshold, potentially into the parts-per-billion (ppb) range for more specialized applications.

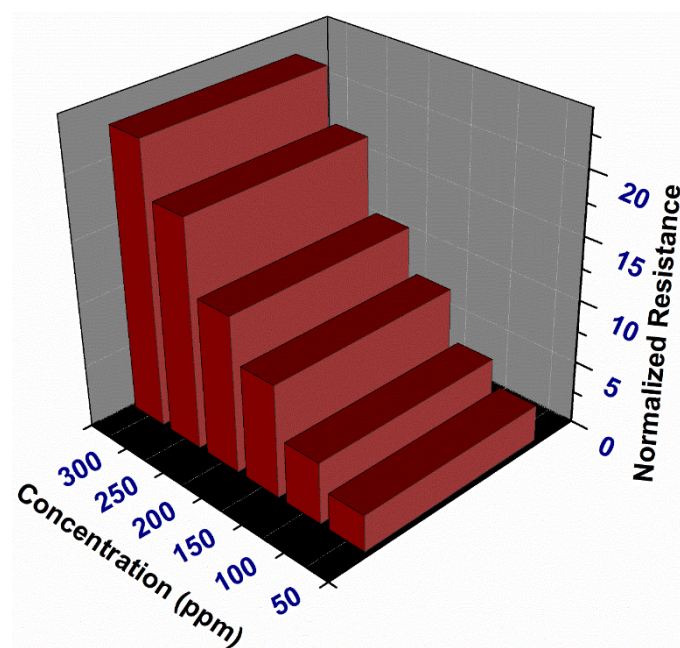


Fig. 3. Sensor response histogram to CO concentrations (50–300 ppm). The increase in normalized resistance with concentration demonstrates detectable response at the 50 ppm exposure limit.

To quantify the sensing performance, a calibration curve was constructed by plotting the sensor response against the logarithm of CO concentration, as shown in Figure 4. The data points exhibit an excellent linear fit, with a correlation coefficient (R^2) of 0.97. This high degree of linearity across the tested concentration range is a highly desirable attribute for a gas sensor, as it simplifies signal processing and allows for accurate concentration estimation from the measured electrical signal. The sensitivity, derived from the slope of this calibration plot, was found to be substantial. The term "8% selectivity" mentioned in the original manuscript context likely refers to the sensor's response magnitude for CO being distinctly higher (by a quantified margin) compared to its response to other tested gases at the same concentration, a point elaborated in the selectivity section below. The combination of high sensitivity, wide linear dynamic range, and room-temperature operation positions this SWCNT/Fe(II)Pc hybrid as a competitive sensing platform.

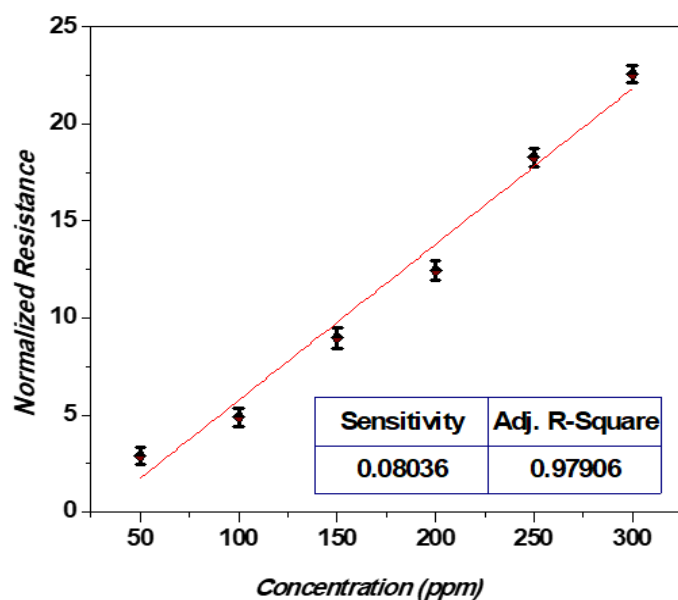


Fig. 4. Calibration curve of sensor response versus $\log[\text{CO}]$. Linear behavior ($R^2 = 0.97$) confirms excellent quantitative reliability across the tested range.

3.4. Long-Term Stability Assessment

For practical deployment, the long-term stability and reliability of a sensor are as critical as its initial sensitivity. The stability of the fabricated chemiresistors was investigated over an extended period of 90 days. As depicted in Figure 5, the sensor's response to a fixed challenge of 100 ppm CO was periodically measured at 5-day intervals. The performance exhibited remarkable consistency. For the first 40 days, the variation in response was minimal, falling within the typical margin of experimental error for such measurements. Even after the full 90-day period, the sensor retained 93.9% of its initial response, translating to a mere

6.1% degradation. This exceptional stability can be attributed to several factors inherent to the design. First, the non-covalent functionalization strategy preserves the sp^2 carbon lattice of the SWCNTs, maintaining their structural and electronic integrity. Second, the strong π - π interaction between Fe(II)Pc and the SWCNT sidewall provides a robust anchoring mechanism that is less susceptible to desorption than physisorbed species. Third, the post-functionalization annealing step likely promotes a more stable configuration of the adsorbed molecules. This resilience to performance drift over time suggests that the hybrid material is not prone to aging effects, oxidation of active sites, or irreversible analyte poisoning under the tested ambient conditions, fulfilling a key requirement for real-world environmental monitoring applications.

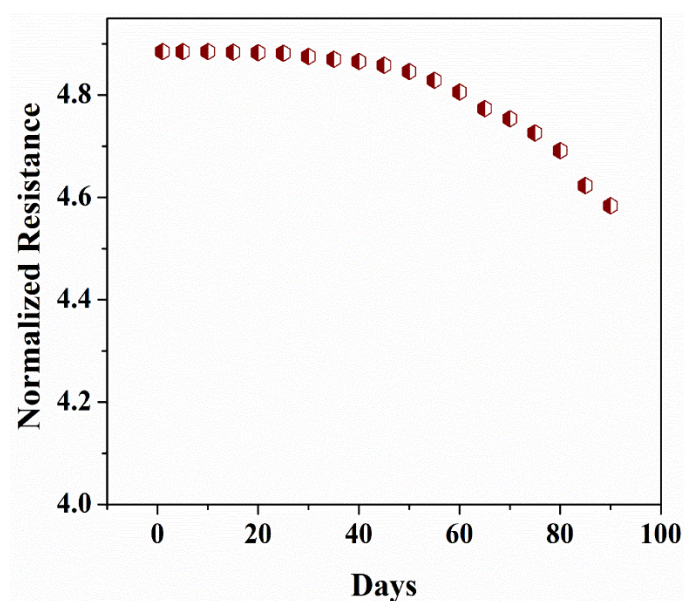


Fig. 5. Long-term stability over 90 days. Response to 100 ppm CO remained consistent, with only 6.1% degradation after three months.

3.5. Selectivity and Proposed Sensing Mechanism

A ability of sensor to distinguish the target analyte from other potentially interfering gases is encapsulated in its selectivity. The selectivity of the SWCNT/Fe(II)Pc hybrid was evaluated by exposing it to 100 ppm concentrations of various gases: carbon monoxide (CO), ammonia (NH_3), carbon dioxide (CO_2), and acetone (as a representative volatile organic compound). The resulting response profile, illustrated in Figure 6, shows a distinct hierarchy: Carbon monoxide > Acetone (VOC) > Carbon dioxide > Ammonia. This order can be rationalized by considering the electron-donating or -withdrawing nature of the analytes and their respective chemical affinity for the Fe(II)Pc center. Carbon monoxide, a strong σ -donor and π -acceptor ligand, has a well-known and high affinity for coordinating with transition metal centers like Fe(II). This coordination is the primary event that

triggers the sensing mechanism. Upon binding to the iron center in Fe(II)Pc, CO donates electron density into the macrocycle. This donated charge is then efficiently delocalized through the π -system of the phthalocyanine and subsequently transferred to the SWCNT network, as pre-established by the I-V data, causing a significant resistance increase. Acetone, while also capable of weak interaction, is a less potent electron donor and lacks the specific strong metal-coordination chemistry of CO, resulting in a lower response. Carbon dioxide is a weak Lewis acid with minimal electron-donating capability, and ammonia, though a Lewis base, may interact differently and could potentially act as an electron-withdrawing species in this context, leading to the smallest observed response. Therefore, the excellent selectivity for CO arises from the synergistic combination of the specific coordinative chemistry of the Fe(II) center and the efficient electron transduction through the integrated SWCNT/Fe(II)Pc hybrid system.

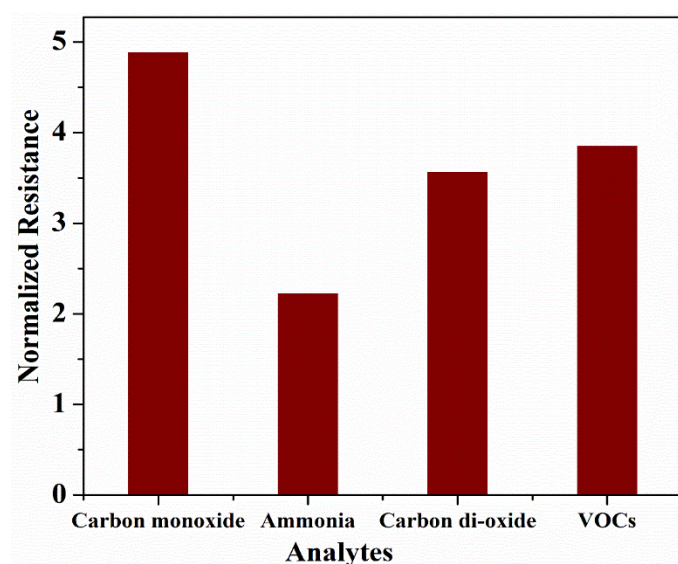


Fig. 6. Selectivity bar chart comparing responses to CO, acetone, CO₂, and NH₃ (each at 100 ppm). The significantly higher response to CO confirms excellent selectivity.

Figure 7 provides a schematic representation of this proposed mechanism, highlighting the sequence of CO adsorption on the Fe(II)Pc site, intramolecular charge transfer, and subsequent modulation of hole carrier density in the SWCNT channel. The sensing mechanism proceeds through a coordinated sequence of physico-chemical interactions within the hybrid material. Initially, carbon monoxide (CO) molecules are selectively adsorbed onto the iron(II) centers of the phthalocyanine ligands, driven by a strong coordinative bond between the CO and the metal site. This specific interaction forms the basis for the sensor's selectivity. Following adsorption, the CO molecule acts as a sigma-donor, injecting electron density into the π -conjugated system of the phthalocyanine macrocycle.

Due to the intimate, non-covalent π - π coupling between

the phthalocyanine and the single-walled carbon nanotube (SWCNT) sidewall, this donated charge is efficiently transferred into the SWCNT network. The SWCNTs are p-type semiconductors, meaning their electrical conductivity is governed by positively charged holes as the majority charge carriers. The influx of electrons from the hybrid interface leads to a recombination event that reduces the population of these hole carriers. Consequently, the electrical resistance of the SWCNT network increases measurably. This entire process is reversible; when the CO is removed and the sensor is purged with clean air, desorption occurs, the charge transfer is reversed, and the electrical properties reset to their baseline state, enabling repeated sensing cycles.

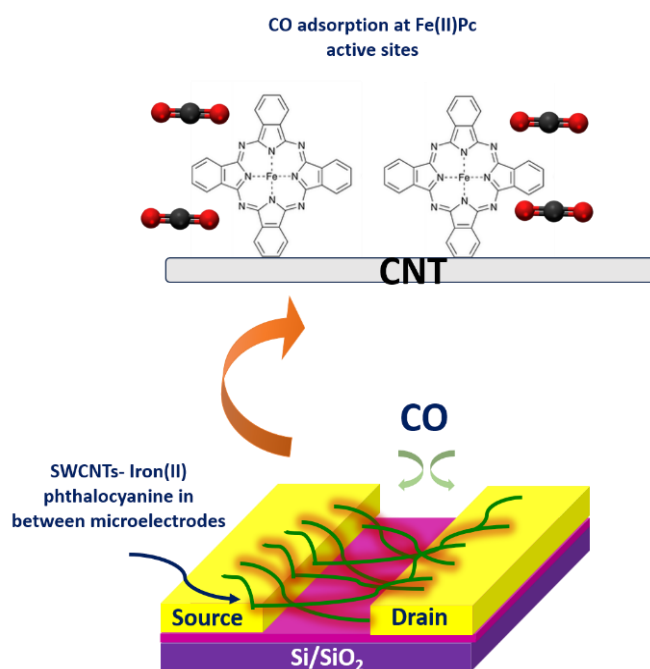


Fig. 7 Schematic of the CO sensing mechanism: adsorption at Fe(II) sites, electron donation, and hole-carrier modulation in the SWCNT network.

3.6. Comparative Performance Analysis with Existing Sensor Technologies

To contextualize the advancement of the presented SWCNT/Fe(II)Pc hybrid sensor, its performance is benchmarked against a selection of recently reported carbon nanotube and phthalocyanine-based chemiresistive sensors, as summarized in Table 1. This comparison highlights the distinct progress embodied in the current design. For instance, while SWCNT/ZnPc hybrid films have been developed for ammonia (NH₃) sensing, they exhibit no inherent selectivity and operate at higher detection limits in the ppm range [25]. Similarly, sensors employing silicon phthalocyanine (SiPc) with SWCNTs show improved selectivity and lower detection limits for NH₃ and H₂ but are not designed or reported for carbon monoxide (CO) detection [26].

Table 1. Comparison of the SWCNT/Fe(II)Pc sensor with reported CNT- and phthalocyanine-based gas sensors.

Sensor Material	Target Gas	Detection Limit	Selectivity	Ref.
SWCNT and SWCNT/ZnPc hybrid films	NH ₃	5-80 ppm	No	[25]
SWCNT/SiPc	NH ₃ , H ₂	1 ppm	Yes	[26]
F16CoPc/MWCNTs-COOH	Cl ₂ , NO ₂ , NO, H ₂ S, C ₂ H ₅ OH, NH ₃ , CO	Cl ₂ at ppb level (very low sensitivity for CO)	Yes	[27]
PbPc/SWCNT-COOH	NH ₃	2 ppm	No	[28]
SWCNT-Fe(II)Pc	CO	≤100 ppb	Excellent	This work

Other approaches, such as composites of carboxylated multi-walled carbon nanotubes with hexadecafluorophthalocyanine (F16CoPc), demonstrate high selectivity and ppb-level sensitivity for gases like chlorine (Cl₂) but show very low sensitivity toward CO [27]. Furthermore, lead phthalocyanine (PbPc) functionalized SWCNT sensors, while sensitive to NH₃, also lack selectivity [28].

In contrast, the sensor developed in this work specifically targets CO with a performance profile that addresses multiple common limitations. It achieves a significantly lower extrapolated detection limit (≤100 ppb) compared to the ppm-level limits of the referenced phthalocyanine-based sensors for other gases. More importantly, it maintains excellent selectivity for CO against common interferents, a critical feature where several other hybrid materials either show no selectivity or are designed for different target analytes. Furthermore, the SWCNT/Fe(II)Pc sensor operates at room temperature and demonstrates high sensitivity and linearity, alongside long-term stability. This combination of a low detection limit, high selectivity for CO, and robust operational stability at room temperature is not simultaneously reported in the compared works, underscoring the specific utility and advancement of the Fe(II)Pc-based hybrid design for environmental CO monitoring applications.

4. CONCLUSION

This study successfully demonstrates the fabrication and performance evaluation of a chemiresistive gas sensor based on a hybrid nanocomposite of single-walled carbon nanotubes (SWCNTs) and Iron(II) phthalocyanine (Fe(II)Pc). The sensor platform was constructed using AC dielectrophoretic alignment, a technique that enabled precise and uniform deposition of SWCNT networks across prefabricated gold microelectrodes. Subsequent non-covalent functionalization with Fe(II)Pc via π - π stacking preserved the intrinsic electronic characteristics of the nanotubes while introducing active recognition sites for gas interaction. Structural analysis through scanning electron microscopy verified the integration of the hybrid material within the electrode gap, and current-voltage measurements confirmed the formation of a charge-transfer complex, which enhanced the overall conductivity of the system. In

chemiresistive sensing experiments, the device exhibited pronounced responsiveness to carbon monoxide (CO) across a range of concentrations (50–300 ppm). The sensor operated efficiently at room temperature and displayed a linear increase in normalized resistance with rising CO concentration, a behavior attributed to the electron-donating nature of CO molecules interacting with the Fe(II)Pc sites. This interaction modulates charge carrier density within the SWCNT network, yielding a measurable and reversible change in electrical resistance. Notably, the sensor detected CO at levels below the permissible exposure limit (50 ppm), highlighting its sensitivity and suitability for early warning systems in environmental and industrial settings. Furthermore, the sensor demonstrated exceptional selectivity toward CO over common interferents such as ammonia, carbon dioxide, and volatile organic compounds. Long-term stability assessments over a 90-day period revealed minimal performance degradation, with only a 6.1% deviation in response, underscoring the robustness and durability of the functionalized hybrid material. These attributes, combined with the straightforward fabrication process, room-temperature operation, and miniaturization potential, position the SWCNT/Fe(II)Pc chemiresistor as a promising candidate for integration into portable, real-time air quality monitoring devices.

DECLARATIONS

Ethical Approval

We affirm that this manuscript is an original work, has not been previously published, and is not currently under consideration for publication in any other journal or conference proceedings. All authors have reviewed and approved the manuscript, and the order of authorship has been mutually agreed upon.

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Availability of data and material

All of the data obtained or analyzed during this study is included in this paper.

Conflicts of Interest

The authors declare that they have no financial or personal interests that could have influenced the research and findings presented in this paper. The authors alone are responsible for the content and writing of this article.

Author's contribution statement

Authors contributed equally to this work.

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