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# **Recent Advances in Conducting Polymers Doped with Metal Oxides for Enhanced Gas Sensing Applications**

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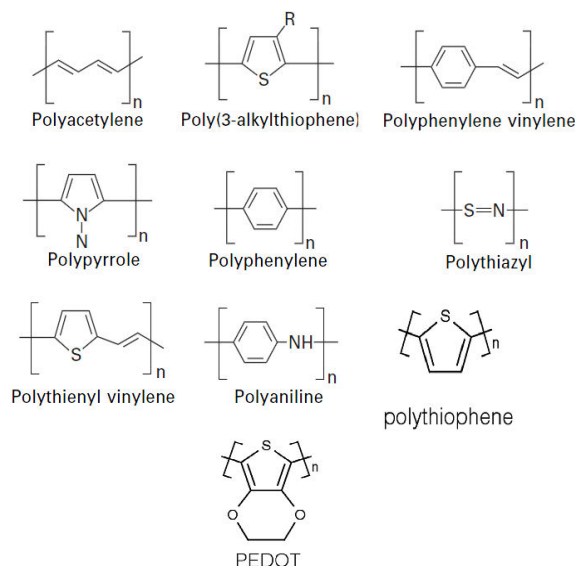
**ABSTRACT:** Gas sensing technology has become increasingly vital in addressing environmental, industrial and healthcare challenges. Conducting polymers have emerged as promising materials for gas sensors due to their unique electrical, chemical and mechanical properties. However, their performance is often hindered by limitations such as poor stability and reduced sensitivity. To address these challenges, the incorporation of metal oxides as dopants in conducting polymers has gained significant attention. This review explores recent advancements in the development of conducting polymers doped with metal oxides, highlighting the synergistic effects that enhance gas sensing capabilities.

**KEYWORDS:** Gas, sensor, polymer, metal, oxide.

## **I. INTRODUCTION**

The discovery of conductive polymers has opened up new opportunities for researchers worldwide, despite the fact that polymers are generally considered to be non-conductive. The modern exploration of electrical conductivity in conjugated polymers is generally recognized to have begun in 1977, marked by a publication from researchers at the University of Pennsylvania discussing the doping of polyacetylene. Although earlier studies date back to World War II and electrochemical synthesis was reported as early as the nineteenth century, the Nobel Prize in Chemistry in 2000 was awarded to Heeger, MacDiarmid, and Shirakawa for their revolutionary contributions to this field [1-6]. A significant aspect of research on conjugated polymers has been the evolving emphasis on technological applications, which has shaped the direction of research over the past 30 years by prioritizing certain physical properties. Initially, in the early 1980s, the primary focus was on achieving high electrical conductivity. Ambitious proposals were made to replace traditional copper wiring in applications such as printed circuit boards, household electrical systems, and even power distribution grids with lightweight, cost-effective polymer conductors. However, as issues related to processability, conductivity limitations, and environmental stability became apparent, these plans were ultimately abandoned. In niche applications, electrical conductivity remains a critical feature.

Fig 1: Structures of Some Conducting Polymers

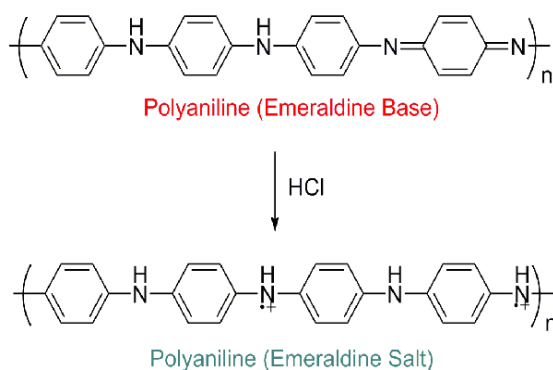


## II. POLYANILINE AND POLYPYRROLE: A PROMINENT CLASS OF CONDUCTING POLYMERS

### Polyaniline:

Polyaniline is a notable conducting polymer, alongside other polymers like polypyrrole. It is synthesized by oxidizing aniline salt, its corresponding monomer, to form a polymer with a standard conductivity, functioning as an organic semiconductor. The combination of certain factors, along with its ease of preparation and cost-effective production of nanoscale morphologies, has made it the subject of increasing research and patents. Polyaniline's history dates back to the 1830s-1840s when researchers studying the molecular structure of indigo through dry distillation discovered aniline. This novel chemical's features, including its oxidation leading to a green product now known as polyaniline, were investigated. The oxidation chemistry of aniline is complex, and by 1910, various oxidation products were identified, such as leucoemeraldine, emeraldine, and pernigraniline, based on their oxidation levels. These were initially thought to be linear aniline octamers. The polymeric nature of these oxidation products was recognized in the 1960s, but the nomenclature for octamers continued to be used in modern research. Once the oxidant is depleted and the reaction ends, it transitions to the emeraldine form. When emeraldine salt is transferred to an alkaline environment, it converts to the corresponding blue emeraldine base. The shift from a conducting to a non-conducting form is significant.

Fig 2: Chemical Structure of Polyaniline



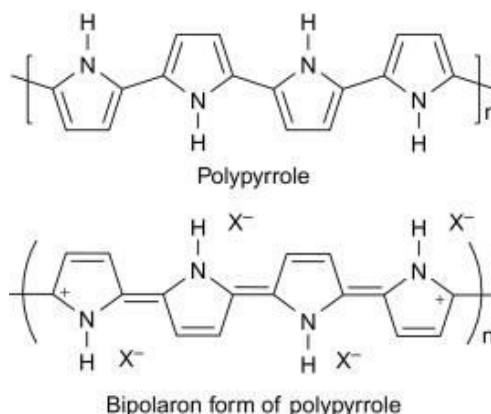


A lower polymerization temperature tends to result in higher molecular weights. The polymer fraction is often associated with oligomers produced during the early stages of aniline oxidation. The oxidation of aniline generates oligomers, a soluble polyaniline fraction, and an insoluble component, with the proportions of each varying depending on the reaction conditions [7-11]. Likewise, ammonia ( $\text{NH}_3$ ) is the most extensively researched gas for PANI sensors. Diverse architectures, including film, thin film, nanofibers, nanofibrous thin film, and nanowire, yielded nearly identical reactions, ranging from 1 to 3, to various gases.

#### Polypyrrole:

Polypyrrole (PPY) is an electrically conductive, biocompatible polymer with a range of potential applications in fields. PPY can be fabricated using simple, cost-effective methods, including chemical and electrochemical techniques. Chemical polymerization of PPY allows for a wider range of oxidizing agents compared to other conducting polymers. In recent years, the electrodeposition of PPY on metallic substrates has gained considerable attention because it allows for precise control over the coating's thickness and morphology. At elevated concentrations of 10,000 to 12,500 ppm, the PPY based sensor responses exhibit minimal variation, ranging from 1.3 to 2.6. The majority of investigations produced low responses (1.0–1.5) despite the fabrication of diverse materials for the active layer into films, nanofibers, nanowires, nanotubes, nanoparticles, and nanoribbons. Surface shape significantly influences the gas sensing efficacy of conducting polymers, particularly at the nanoscale. When the dimensions of most examined materials are diminished to the nanoscale, numerous novel or enhanced features often arise. This occurs across a broad concentration range of 100 to 110,000 ppm, irrespective of the various analytes examined. A comparable instance was noted where sensors based on various architectures, including films, nanowire arrays, and nanosheets, were developed but demonstrated nearly identical responses to a range of gases, often between 1 and 1.9.

Fig 3: Chemical Structure of Polypyrrole



There is a growing body of material regarding the use of PPy as a possibly electrically addressable substrate for tissue or cell support. The development of PPy is contingent upon its electrical properties; if it were non-conductive, its growth would be self-restricting, resulting in extremely thin films, similar to polyphenol and its derivatives. Temperature and pH influence the resultant film [12].

### III. METAL OXIDE-POLYMER GAS SENSORS

Various metal and metal oxide composites have also been employed to enhance the response and recovery kinetics of sensing materials. Recent studies have explored chemiresistor gas sensors for  $\text{NH}_3$  using nanostructured materials. These CP/metal oxide nanocomposites exhibited  $\text{NH}_3$  detection at concentrations as low as 50 ppb in air, showing better performance than for methanol and ethanol vapors. Researchers have also developed a sustainable chemical synthesis process for  $\text{P}_3\text{HT}/\text{CdSe}$  (QDs) nanocomposites, which when illuminated with monochromatic light at 600 nm, the sensor's charge transfer was enhanced, leading to improved responsiveness and faster recovery times [13-29].

Metal oxide nanoparticles are crucial for sensing applications because of their adjustable electrical, magnetic and thermal characteristics. These materials are employed in many applications, including gas sensors, humidity sensors,

and biosensors, owing to their elevated sensitivity and selectivity for various analytes. Metal oxide nanostructures are very advantageous in electronics and optoelectronics, encompassing capacitors, transistors, and transducers. Tin Oxide (SnO, SnO<sub>2</sub>), Zinc Oxide (ZnO), and Titanium Dioxide (TiO<sub>2</sub>) are prevalent metal oxide compounds with significant properties for sensing applications.

Energy bands in materials are essential for the design and execution of electronic devices, and metal oxides are regarded as attractive due to their advantageous energy band structure. Energy bands arise from the quantum mechanical behavior of electrons in atoms, influencing the electrical, optical, and catalytic qualities activated by diverse electrical, thermal, and optical perturbations. Tin oxide (SnO, SnO<sub>2</sub>) is a p-type semiconductor characterized by a direct bandgap of 2.5-3.0 eV. ZnO exhibits a substantial specific surface area, biocompatibility, chemical and photochemical stability, electrical characteristics including a low dielectric constant and excellent light transmittance, non-toxicity, ease of synthesis, and exceptional physiochemical properties. ZnO is an exceptional and economical material for application in gas sensors, chemical sensors, and humidity sensors. Titanium dioxide (TiO<sub>2</sub>) is an n-type semiconductor with a broad energy bandgap, rendering it very suitable for use in gas sensors, environmental monitoring sensors, humidity sensors, and biosensors. TiO<sub>2</sub> can be doped to enhance performance. Consequently, metal oxide nanoparticles exhibit advantageous characteristics for sensing applications, including high sensitivity, rapid reaction and recovery times, exceptional repeatability and stability, as well as cost-effectiveness. Comprehending energy bands and their significance in sensing applications is crucial for the design and implementation of electronic devices.

The electrical conductivity of metal oxide materials varies due to interactions with the ambient atmosphere. Gas sensors utilizing field-effect transistors (FET) are classified according to the sensor type. Chemiresistive gas sensors employ semiconducting metal oxides (SMOs) because of their adjustable characteristics and responsiveness to the environment being analyzed. The operational theory of a conductometric metal oxide-based gas sensor is straightforward, although the gas sensing mechanism is intricate. Three autonomous aspects govern sensor and sensing efficacy: receptor functionality, transducer functionality, and barrier elevation. The utility factor is essential in assessing a device's sensing capability. Recent advancements have been achieved with stable and highly selective compositions proven for nitrogen dioxide (NO<sub>2</sub>) detection at low temperatures of approximately 80°C. Photoluminescence (PL) gas sensors operate on the principle of photoluminescence quenching, which generates luminescence from photo-induced electron/hole pairs and/or intrinsic defects in metal oxide materials like ZnO. These materials exhibit alterations when subjected to target gases, attaining remarkable selectivity and sensitivity. The sensing of ethanol gas using PL-based methods with ultrafine 1D WO<sub>3</sub> nanorods, measuring 10-200 nm in diameter, has been examined. The results indicate that when the nanorods are subjected to trace amounts of ethanol gas, the spectra of the nanorods under UV light exhibit considerable intensity change. WO<sub>3</sub>-based ethanol gas sensing exhibited a sensitivity detection limit of 100 ppm, as indicated by variations in PL spectra. Table 1 provides a review of PANI and PPy polymer doped with metal oxides for gas sensor applications.

Table 1: PANI and PPy Composites for Gas Sensing Applications

Conducting Polymer	Metal Oxide Dopant	Target Gas	Synthesis Method	Sensing Performance	Reference
PANI	Zinc Oxide (ZnO)	Ammonia (NH <sub>3</sub> )	In-situ chemical oxidative polymerization	Enhanced sensitivity at room temperature	Zoshki et al. (2017) [30]
	Titanium Dioxide (TiO <sub>2</sub> )	Hydrogen (H <sub>2</sub> )	In-situ chemical oxidative polymerization	Improved sensitivity and selectivity	Srivastava et al. (2010) [31]
	Tin Oxide (SnO <sub>2</sub> )	Ammonia (NH <sub>3</sub> )	in-situ polymerization method	Enhanced sensitivity and rapid response	Kulkarni et al. (2018) [32]
	Bismuth Oxide (Bi <sub>2</sub> O <sub>3</sub> )	Liquefied Petroleum Gas (LPG)	Chemical Route	Improved sensing response	Nemade and Waghuley (2013) [33]
	Cobalt Oxide	Carbon	ultrasound assisted	Enhanced	Mishra et al.

	(Co <sub>3</sub> O <sub>4</sub> )	Monoxide (CO)	coprecipitation method	sensitivity and selectivity	(2016) [34]
	Copper Oxide (CuO)	Methanol (CH <sub>3</sub> OH)	mechanical mixing method	High sensitivity and stability	Pattar et al. (2021) [35]
	Iron Oxide (Fe <sub>2</sub> O <sub>3</sub> )	Methanol (CH <sub>3</sub> OH)	Successive ionic layer adsorption and reaction technique.	Improved selectivity and response time	Zhang et al. (2019) [36]
	Manganese Oxide (MnO <sub>2</sub> )	Ammonia (NH <sub>3</sub> )	Hydrothermal synthesis	Enhanced sensitivity and stability	Umar et al. (2024) [37]
	Cerium Oxide (CeO <sub>2</sub> )	hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )	in situ oxidative polymerization process	High sensitivity and rapid response	Hussein et al. (2022) [38]
	Cobalt Ferrite (CoFe <sub>2</sub> O <sub>4</sub> )	Ammonia (NH <sub>3</sub> )	in situ chemical oxidative polymerization method	Enhanced sensitivity and selectivity	Alharthy and Saleh (2021) [39]
PPy	Tungsten Oxide (WO <sub>3</sub> )	Ammonia (NH <sub>3</sub> )	pulsed-laser deposition (PLD) and matrix-assisted pulsed-laser evaporation (MAPLE)	exceptional gas-sensing performance	Filipescu et al. (2023) [40]
	Zinc Oxide (ZnO)	Ammonia (NH <sub>3</sub> )	sol-gel technique	Enhanced sensitivity and selectivity	Paliwal et al. (2021) [41]
	Tin Oxide (SnO <sub>2</sub> )	Ammonia (NH <sub>3</sub> )	Chemical polymerization	High sensitivity at room temperature	Gahlot et al. (2022) [42]
	TiO <sub>2</sub> /ZnO	Ammonia (NH <sub>3</sub> )	Chemical polymerization	Enhanced sensitivity and fast response	Wang et al. (2009) [43]
	Iron Oxide (Fe <sub>2</sub> O <sub>3</sub> )	NO <sub>2</sub>	spin coating method	High sensitivity and rapid response	Navale et al. (2014) [44]
	Molybdenum Disulfide	NO <sub>2</sub>	Chemical polymerization	greater sensitivity	Zhao et al. (2024) [45]
	Graphene oxide	Carbon monoxide (CO)	in situ polymerization process	Enhanced selectivity and stability	Faree et al. (2021) [46]

Metal oxide semiconductors have enhanced the sensing performance of gas sensors by synthesis processes that yield increased surface area and pore dimensions. Doping with elements such as Rh, Ag, Si, and Pd has demonstrated an improvement in the detecting performance of metal oxide gas sensors. Humidity sensors, akin to gas sensors, possess comparable characteristics including elevated sensitivity, exceptional stability, and consistent response times. Commonly researched metal oxide compounds for humidity sensing encompass ZnO, SnO<sub>2</sub>, TiO<sub>2</sub>, CuO, and WO<sub>3</sub>. Humidity sensors can be categorized based on their design and operational approach as resistive, capacitive, or impedance sensors. Researchers have recently examined a sensor CuO/Ti<sub>3</sub>C<sub>2</sub>TX MXene nanosheet. The results indicated a brief reaction time of 0.5 seconds, a recovery time of 1 second, a low hysteresis value, and excellent repeatability, demonstrating significant potential for respiratory monitoring and environmental detection owing to its remarkable characteristics [47].

#### IV. CONCLUSION

The integration of metal oxides into conducting polymers has demonstrated remarkable potential in enhancing the performance of gas sensors. The synergistic interaction between conducting polymers and metal oxides leverages their

complementary properties, such as the superior adsorption and catalytic capabilities of metal oxides.

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