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CHAPTER 9

Synthesis Pathways of Conducting Polymers and Nanocomposites for Hazardous Chemical Detection

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Abstract: The field of Volatile Organic Chemical (VOC) sensors is rapidly growing, driven by the increasing demands of modern advanced technologies. Conducting polymers and their nanocomposites play a crucial role as chemical sensor materials, offering significant advantages over traditional inorganic semiconductors. The nano-sized particles in polymer-based sensing devices enhance both sensitivity and selectivity due to various interactions between the target chemicals and the polymer nanocomposite. Currently, polyaniline (PANI), Poly aminophenol, poly phenylenediamine and its nano composite are widely studied in the field of sensing materials. However, due to their inherently low conductivity, they are not effective standalone sensors. To overcome this limitation, silver, copper and Carbon nanotube (CNT) nanocomposites integrated with conjugated polymers have emerged as excellent sensing materials. This review highlights recent advancements in the development and design of conjugated polymer

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nanocomposite (CPNP)-based sensors, emphasizing their potential for highly selective and sensitive chemical detection.

Keywords: Conducting Polymer, Polymer nano composite, Polyaniline, Poly-phenylenediamine, Hazardous chemical sensor

Introduction

In today's lifestyle, the prevalence of diseases such as diabetes, cancer, obesity, aging-related issues and degenerative disorders is increasing. Antioxidants play a crucial role in combating these conditions. Among natural antioxidant-rich beverages such as tea, coffee, and wine, wine is particularly significant in helping prevent these diseases.[1] Some type of wines reduces the incidence of heart attacks and high cholesterol level.[2] In rural areas, people produce wine from natural sources using the fermentation process, a method also followed in manufacturing industries. During fermentation, it is crucial to control the purity of ethanol, as even small amounts of other alcohols can cause health issues such as vertigo, headaches, nausea, and vomiting. Methanol and isopropanol are common by-products of fermentation, and their presence must be carefully monitored to ensure the safety of the final product. The consumption of 20 ml of methanol can cause blindness and while 60 ml is usually lethal if not treated.[3] Driving under the influence of alcohol (ethanol) causes road accident in every year.[4] So methanol is very toxic and its environmental exposure limit is 200 ppm as recommended by various international organization (NIOSH, OSHA and ACGIH).[5] Therefore, the sensing and determination of alcohol concentration, particularly methanol, is crucial. P. Kar *et al.* reported the sensing of aliphatic alcohols using sulfuric acid-doped poly(m-aminophenol) film. However, their study did not achieve selective sensing when detecting alcohols in a mixture.[6] Poly(o-phenylene diamine) also acts as a good sensing material towards methanol, ethanol and higher alcohol but the polymer do not detect selective sensing among the mixture of alcohols.[7] Acid-doped polymer sensing materials are effective for sensing applications. However, a key concern is the physical strength of the polymer film after acid doping. Typically, acid doping reduces the film's strength, leading to increased brittleness in the polymer matrix. In contrast, nanoparticle-doped polymer films maintain their strength, offering a more durable alternative for sensing applications. [8,9] Polymer nanocomposites serve as excellent sensing materials due to the high surface area of nanomaterials, which enhances their sensitivity. Therefore, the development of polymer nanocomposite-based sensing devices is crucial for industrial applications. Some of the examples of conducting polymer are poly(o-phenylenediamine) (PoPD), polyaniline (PANI), polythiophene (PTh), poly(m-aminophenol) (PmAP), polypyrrole (PPy), and polyfuran (PFu), etc as shown in Figure 1.[10-14]

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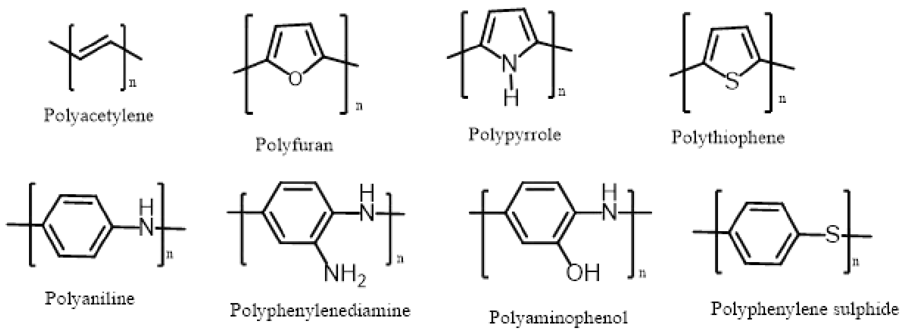

Fig. 1. Molecular structures of some important conducting polymers

In the alcohol manufacturing industry, detecting methanol concentration within alcohol mixtures is crucial for safety and quality control. This review article describes the synthesis route, volatile organic compound (VOC) sensing, and the sensing mechanism of polymer nanocomposites. Heavy metal ion contamination in industrial wastewater poses a significant global threat to human health and the environment, primarily because of the high mobility and toxicity of these pollutants in aquatic ecosystems. As industries like chemical manufacturing, mining, metal plating, tanning, fertilizer production, battery manufacturing, pesticide formulation and paper production continue to grow rapidly, they often release heavy metals either directly or indirectly into rivers, lakes, and marine environments. The application of conducting polymer in various field are shown in Figure 2.

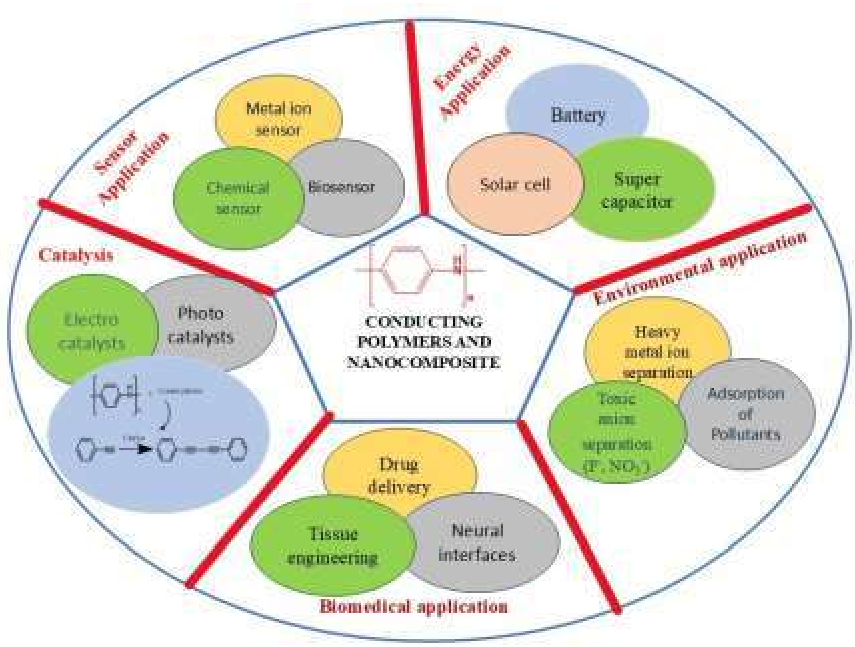

Fig. 2. Some application of Conducting polymer and nano composite

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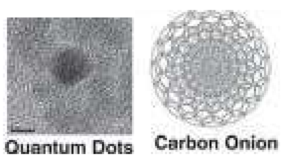
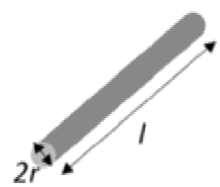
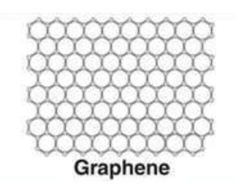
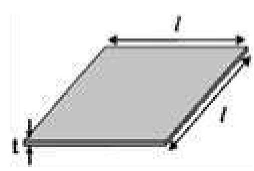
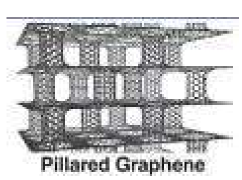
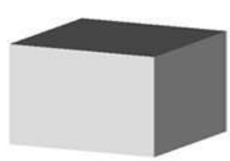
Synthesis of Polymer nano composite

Nanoparticles are defined as particles with at least one dimension in the nanometer range (approximately 10^{-9} meters). When materials scale down from the microscale to the nanoscale, they exhibit significant changes in their electrical, optical, physical, and chemical properties [15]. These changes are primarily attributed to the high aspect ratio and increased surface area of nanomaterials. Since many key material properties are strongly influenced by surface characteristics, polymer nanocomposites offer a wide range of applications. Table 1 below presents various geometries of nanoparticles along with their corresponding surface area-to-volume (aspect) ratios.

Table 1: Types of Nanomaterials According to Aspect Ratio with Common Examples

Nanomaterials type	Figure	Aspect ratio	Common example
Nanoparticle, Quantum dots	 (0-dimensional)	 $3/r$	metallic or metal oxide quantum dots and nanoparticles (Cu, Ag and Au nano particle)
Nano-Fibrous	 (1-dimensional)	 $2/r + 2/l$	SWCNT, MWCNT and Carbon nanofibers
Layered nanomaterials	 (2-dimensional)	 $2/t + 4/l$	Graphene, Nano clay, MoO_3
Structured nanomaterials	 (3-dimensional)	 Depends on the particular structure	Pillared graphene, Metal organic Frameworks

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Polymer nanocomposites were synthesized using physical, chemical, and electrochemical methods, as illustrated in Figure-3. In the physical preparation method, nanomaterials are incorporated into a pre-synthesized conjugated polymer matrix by simple mixing. [16,17] An example of physically synthesized polymer nanocomposites is the preparation of polyaniline/copper nanocomposite by simple mechanical stirring for 12 hours in water. [18]

In the chemical synthesis process, nanoparticles are incorporated into the polymer matrix using in-situ and ex-situ methods. Verma *et al.* synthesized poly(m-aminophenol) (PmAP)/MWCNT composite via the in-situ method, using aqueous sodium hydroxide (NaOH) and ammonium persulfate (APS) as the oxidant.[19] Similarly, a poly(m-aminophenol) (PmAP) nanocomposite containing 3.0 wt% 3-mercaptopropionic acid (MPA)-functionalized silver nanorods (PmAP/AgNR) was synthesized through in-situ chemical oxidative polymerization of m-aminophenol (mAP) monomer in an aqueous dispersion of Ag-nanomaterials.[20,21]

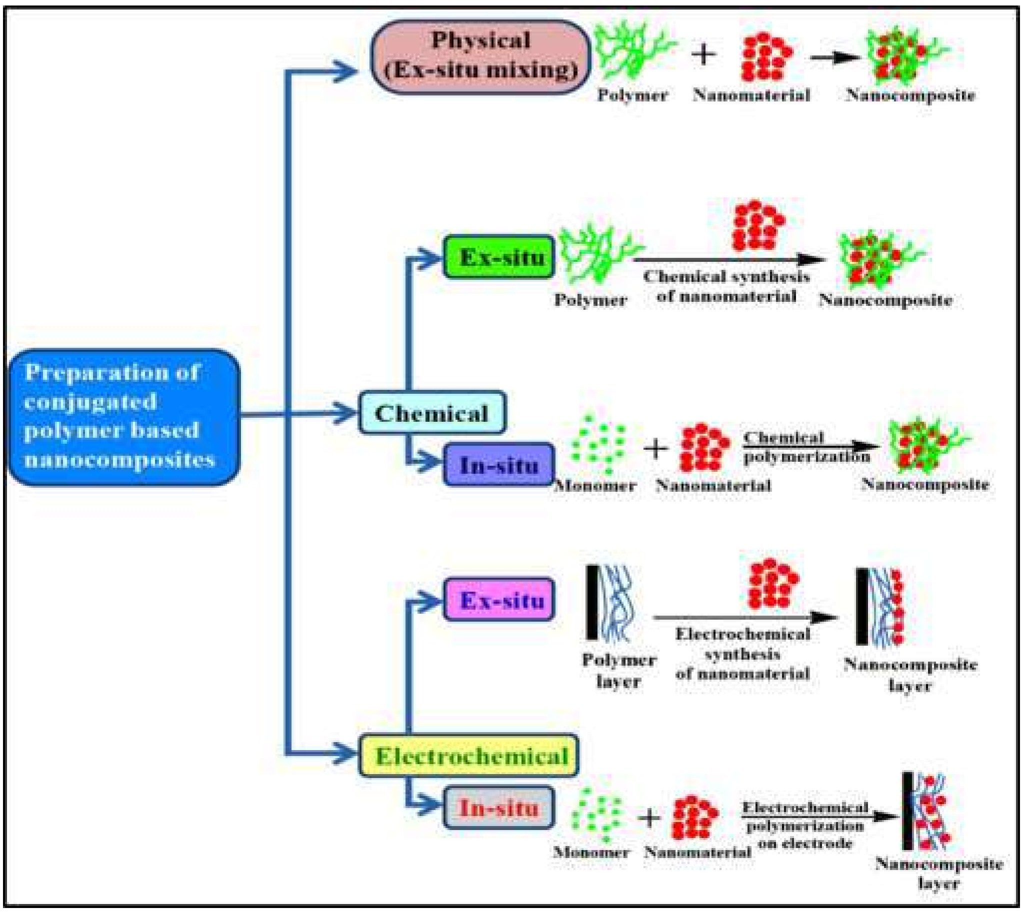

Fig. 3. Physical, chemical and electrochemical approaches to prepare conjugated polymer nanocomposites with metal nanoparticles.

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In the ex-situ process, metal nanoparticles are synthesized within a pre-synthesized conjugated polymer matrix. For example, poly(m-aminophenol)/Cu nanocomposites were prepared using a single-step thermal reduction method during the film casting of the polymer.[9] Another example is poly(m-aminophenol)/Ag nanocomposite, which was prepared by the thermal decomposition of a silver nitrate-ammonia complex during film casting.[22]

The electrochemical synthesis method follows either an in-situ or ex-situ pathway and is a well-established and efficient technique for incorporating metal nanoparticles into conjugated polymers. Initially, ex-situ attempts involved a two-step process, where metal salt was electrochemically reduced on the surface of a conjugated polymer pre-deposited on an electrode. [23]

PmAP/Cu nano composite were synthesized by a single step thermal reduction method using PmAP with copper acetate in DMSO solution at 120^{0}C [9]. In this process, the poly(m-aminophenol) (PmAP) molecule undergoes self-oxidation by donating its lone pair of electrons to Cu(II), which is subsequently reduced to Cu(0) (**Figure-5**).

Sensing performances

A sensor is an instrument that generates an observable signal in the presence of specific analytes, such as biomolecules, toxic and hazardous chemical species, bio-reactive compounds, or biological structures. Based on the type of analyte detected, sensors are generally categorized into three main types: chemical sensors, physical sensors, and biosensors. [24]. The chemical and biosensor, which are very much identical in principle and are commonly classified into four types: (1) electrochemical sensors (2) optical sensors (3) spectrometry sensors and (4) mass sensors. [24, 17]. Schematic representation of simplified sensor set-up consists of a receptor or detection unit, a transducing unit and a signal processing unit as shown in Figure 4.

Fig. 4 Schematic representation of simplified working principle of a sensor

Polymer nanocomposite film with 2 wt% s-MWCNT was selected as lowest resistivity i.e. higher conductivity. PmAP/MWCNT nanocomposite serves as an excellent material for the selective sensing of ethanol, primarily due to the strong hydrogen bonding interactions between ethanol molecules and the polymer nanocomposite, as illustrated in Figure 5.[19] The nanocomposite film exhibited limited response to aliphatic alcohols other than ethanol and methanol. Polypyrrole-ZnO nano composite was found to be

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good sensing materials towards NH_3 vapours even at low concentration of NH_3 gas. [28]. Several conducting polymers and their respective selective sensing materials are summarized in Table 2. From this table, it is evident that polymer and nanocomposite films demonstrate high selectivity for alcohol vapor sensing.

Poly(m-aminophenol)/Cu nanocomposite is also an effective sensing material for methanol. M. Bhuyan et al. reported the selective sensing of methanol vapor using PmAP/Cu nanocomposite, where the sensitivity increased with the Cu content in the polymer matrix, reaching its peak at 3 wt% Cu. Beyond this concentration, no further enhancement in sensitivity was observed, likely due to maximum conductivity being achieved at 3 wt% Cu.[9] The sensing performance of the PmAP/Cu nanocomposite film at 350 ppm alcohol concentration was highest for methanol, while other alcohols remained almost insensitive under the same vapor pressure conditions.

Table 2: Hazardous Chemicals sensing by conducting polymers and its Nano composite

Polymer/polymer nano composite	Sensing materials	Concentration (ppm)	% of Response	References
MWCNT doped Polyaniline and	Chloroform	100 ppm	31%	[25]
poly(m-aminophenol)–silver nanocomposite	Ammonia	100 ppm	88%	[26]
Poly(m-minophenol)/ Amine Groups Functionalized Multi-Walled Carbon Nanotube composite.	Ethanol	150 ppm	67%	[19]
sulfuric acid doped poly(m-aminophenol)	Methanol	173 ppm	30%	[6]
	Ethanol	126 ppm	24%	
Poly(m-aminophenol)/Copper Nanocomposite	Methanol	368 ppm	20%	[9]
Poly(o-phenylenediamine)	Methanol and Ethanol mixture	103 ppm	50%	[27]
Poly(o-phenylenediamine) Nanofiber	Iso-Amyl alcohol	40 ppm	33%	[7]
polypyrrole/ZnO nanocomposites	Ammonia	30 ppm	35%	[28]

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Mechanism of Sensing

The mechanism of sensing depends on the type of sensing material used and the polarity and size of the alcohol molecule. Different alcohol molecules interact differently with polymer nanocomposites due to variations in their size and polarity.

For methanol, which is small in size and highly polar, it interacts strongly with the polymer chain's imine (-C=N) or hydroxyl (-OH) groups via hydrogen bonding. This interaction is further enhanced by Cu nanoparticles, as illustrated in Figure 5(A). However, for larger and less polar alcohols, such hydrogen bonding interactions are absent, making the sensing response weaker. The sensor's response (%) increases with a higher methanol vapor concentration, as shown in Figure 5(B).

Interestingly, the PmAP/Cu nanocomposite film does not effectively sense ethanol, as its larger size prevents incorporation into the polymer matrix chain. Instead, for selective ethanol sensing, the PmAP/MWCNT nanocomposite is a more suitable sensing material. In this case, different types of hydrogen bonding interactions occur: between the -OH groups of poly(m-aminophenol) and ethanol molecules and between the functionalized MWCNT and ethanol molecules. This mechanism is illustrated in Figure 6(A). Additionally, as the ethanol vapor concentration increases, the sensor's response also increases, as depicted in Figure 6(B).

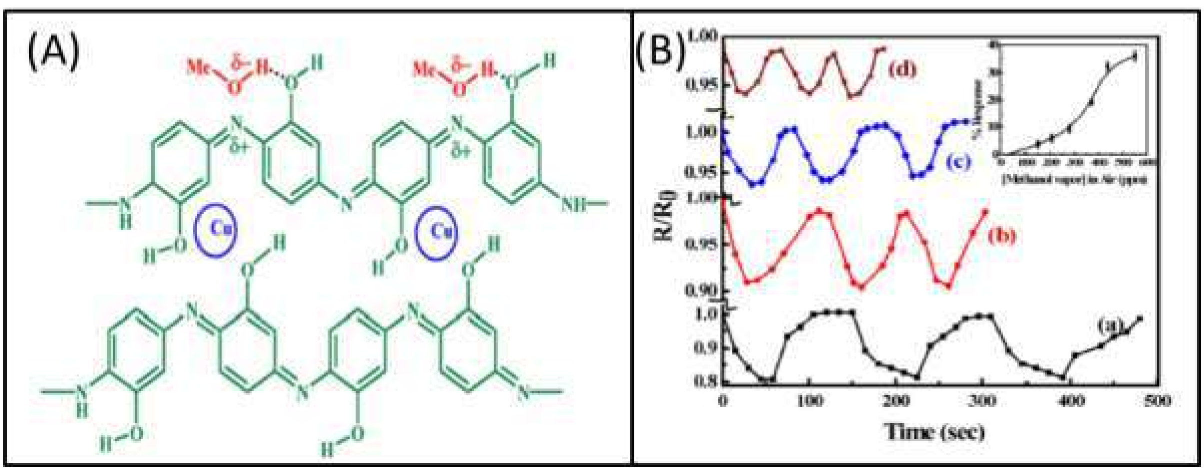

Fig. 5. (A) Mechanism of methanol detection using the PmAP/Cu nanocomposite. **(B)** Sensing % response variation as a function of methanol vapour concentration [9]

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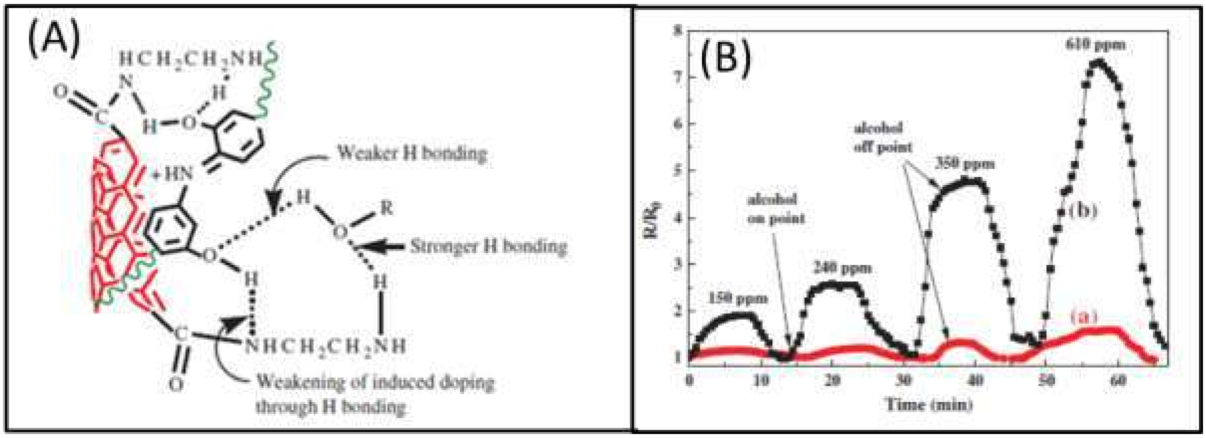

Fig. 6. (A) Alcohol vapor engages in hydrogen bonding interactions with the PmAP/a-MWCNT nanocomposite. **(B)** Sensor response (%) to different concentrations of methanol and ethanol vapor in an air mixture. [19]

Conclusion

Conducting polymers and their nanocomposites serve as excellent sensing materials for volatile organic compounds (VOCs). Among these, polyaniline (PANI) and its functionalized polar derivatives play a crucial role in detecting various volatile organic solvents. From the sensing mechanism, it is evident that different solvents interact uniquely with the polymer chain and nanomaterials. The primary interactions involved in sensing are, dipole-dipole interactions and hydrogen bonding between the solvent molecules and the polymer matrix. Polyaniline with free active functional groups (such as $–NH_2$ or –OH) is particularly effective in sensing methanol, ethanol, and iso-amyl alcohol, as these groups facilitate strong hydrogen bonding interactions with the target analytes. We hope that this review will provide a timely and useful reference for all those interested in conducting polymer based volatile organic compound sensor.

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