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RESEARCH PROGRESS ON POLYTHIOPHENE AND ITS APPLICATION AS CHEMICAL SENSOR

N. Mohd Nurazzi^a, M. M. Harussani^a, S. Z. N. Demon^a, N. A. Halim^a, I. S. Mohamad^b, H. Bahruji^c, N. Abdullah^{a,*}

^a Centre for Defence Foundation Studies, National Defence University of Malaysia, Kem Sungai Besi, 57000 Kuala Lumpur, Malaysia

^b Faculty of Mechanical Engineering, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia

^c Centre of Advance Material and Energy Sciences, Universiti Brunei Darussalam, Jln Tungku Link, BE 1410, Brunei

*Corresponding author: norli.abdullah@upnm.edu.my

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ABSTRACT

The π -conjugated polymers and their derivatives have attracted significant attention in recent decades for research and development as chemical sensor. This is because of their wide range of potential applications especially as an active layer in various electronic devices. The organic structure of these polymers had confer the electronic and material properties and facilitate their processibility. This includes several promising of conjugated polymers such as polyacetylene, polyaniline, polypyrrole, polythiophene (PTh) and etc. Above all, the conjugated polythiophene and its derivatives stand out as one of the promising members of the conjugated polymer family. Due to their unique in electrical characteristics, excellent environmental and thermal stability, low-cost synthesis, and mechanical strength, various procedures have been invoked in order to increase the usability of polythiophene. This includes side chain functionalization of the different derivatives and copolymers, functionalised with carbonaceous materials, and combination of both of these strategies. In this review, focus is on the present conductive polymers, the characteristics and the synthesization of polythiophene and its derivatives, and their applications in chemical sensor are highlighted at the last part.

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Introduction

Since the discovery of the first polymer that can attain a high conductivity in the late 1970s, the field of conductive polymer has made a great progress. Hideki Shirakawa, Alan Heeger and Alan Macdiarmid synthesized different form of oxidized polyacetylene with extraordinary properties such as electrical characteristic and reversible doping-dedoping procedure. Particularly of their collaborative work and development of conductive polymer they were awarded with Nobel Prize in Chemistry in 2000 [1-2]. Polymers such as polyethylene (PE) where the valence electrons are bound in sp^3 hybridized covalent bonds; its "sigma-bonding electrons" have low mobility and do not contribute to the electrical conductivity of the material. Another conductive polymer that has received significant attention since a quarter of century ago is polyacetylene, in which the polymer was found to have a remarkably high conductivity at room temperature when exposed to iodine vapour [3-5].

However, for conductive polymers such as polyacetylene (Fig. 1) which consist of conjugated bonds, the polymers have the continuous sp^2 hybridized carbon centres (alternating double- and single bonds) as backbones. One valence electron on each centre resides in a p_z orbital, which is orthogonal to the other three sigma-bonds. The electrons in these delocalized orbitals have high mobility when the materials undergo doping technique by oxidation (p-doping) or reducing (n-doping) of their conjugated backbones. The conjugated p-orbitals form a one-dimensional electronic band, and the electrons within this band become mobile when it is partially emptied. Other than that, the same polymers can be doped by reduction, which adds electrons to an otherwise unfilled band.

Conductive polymers possess the properties of both organic polymers and inorganic conductors. Organic polymers are built from a covalently linked monomeric units, and these conjugated polymers have the ability to become conductive polymer after being partially oxidized or reduced. The conductivity of is achieved by the presence of deficiency or excessive p-electrons in the polyconjugated chain which also known as doping. Doping is a process to incorporate electrons or holes in the 3-D inorganic semiconductors [3].

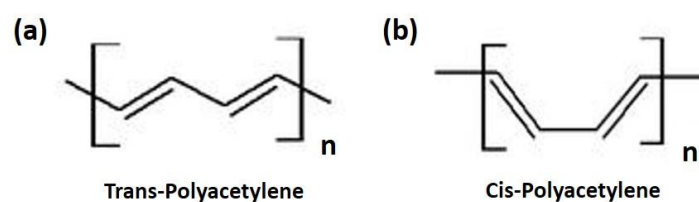
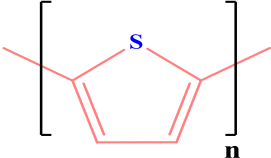

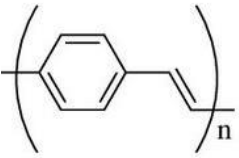
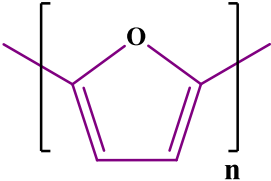


Fig. 1: Chemical structure of trans and cis-polyacetylene

A great deal of effort on the development of the organic conductive polymers has been carried out in the optical and electronic applications. The excellent structural versatility that may be achieved for organic compounds by both high-precision molecular design and an appropriate synthetic method is one of the main reasons for this fast-growing interest. Many conjugated polymers with varying degrees of functionality have been developed, the most common being are polyaniline (PANI), PTh, polypyrrole (PPy) poly (3,4 ethylenedioxy-thiophene) (PEDOT) and polyphenylene [6]. Table 1 illustrates a few of the conductive polymers and their respective conductivities [7-8].

Table 1: Chemical structures of a few of the most important conductive polymers and their respective conductivities

Conductive polymer	Structure	Conductivity (S/cm)
Polyacetylene		~1000
Polyaniline		1-100
Polypyrrole		40-100

Conductive polymer	Structure	Conductivity (S/cm)
Polythiophene		10-100
Poly(<i>para</i> -phenylene)		100-500
Poly(<i>para</i> -phenylene vinylene)		~3
Polyfuran		~80

The interests toward conductive polymers have increased recently for application in electronic devices. The conductive polymers were utilised as a transparent layer for the optical electronics, demonstrating its application for light detections, electrochromic displays and for optical displays. Most of the CPs present are based on the aromatic ring systems. Among the conductive polymers investigated over the past decades, the polymers based on PANI, PEDOT and PPy are important and popular among other conductive polymers due to their low costs, low densities and their light weights. As reported by Somboonsub et al. (2010) these conductive polymers have attracted much attention in organic electronics especially PEDOT which is among of the most popular conductive polymers by showing high conductivity ranging from 10^{-2} to 10^5 Scm^{-1} [9]. The structural versatility that was achieved by both high-precision molecular design and an appropriate synthetic method is the main reason for the fast-growing interest on these organic polymers. The potential applications of organic polymers were reported in various fields such as electromagnetic interference (EMI) shielding [10-11], rechargeable battery [12-13], chemical sensor [14], photovoltaic cell [15-16], separation membranes [17], ion sensing [18], biomolecular immobilization matrices [19], corrosion devices [20-21], microwave absorption [22-23], and many more applications.

Polythiophene

Since the discovery of iodine-doped polyacetylene in 1977 [24], research and development in the field of conducting polymers has made substantial advances. From that, only few conducting polymers have high stability under normal processing conditions that can be incorporated in practical applications [25]. Among them, the leading candidates are PANI, PPy and PTh. Of these, PANI and PPy have been investigated in many applications, such as sensors and photocatalysts [26] etc. Despite being the least studied polymer, PTh has shown many promising applications comparable to both PANI and PPy, such as in electrical or electrochemical applications. The π -conjugated PTh and its derivatives can be utilised as sensors [27-29], organic photovoltaics (OPVs) [30], organic field-effect transistors (OFETs) [31-32], organic light emitting diodes (OLEDs) [33-34], and biomedical fields [35-36].

PTh is a π -conjugated polymer with low-cost synthesis, excellent environmental and thermal stability, mechanical strength, magnetic, and optical properties, and can be used in wide range of applications [8, 37-38]). Fig. 2 shows the chemical structure of regioregular-PTh with the specific attached side chain [39]. A chemical side-chain group can be attached on each thiophene ring along the polymer and an end-group or a secondary copolymer chain can be added to each end of the polythiophene. The π -conjugated backbone of unsubstituted PTh is typically semi flexible in solution. Thus, the polymer chains

tend to aggregate, resulting in poor solubility, low mechanical flexibility, and poor process-ability. In order to overcome these major deficiencies, well-established techniques are: (1) side chain functionalization [40], usually at the β -carbons, (2) synthesis of PTh copolymers with processable polymers [41], and (iii) combination of both aforementioned approaches [42-43].

Table 2 shows the list of chemical structures and properties of thiophene based polymers and its derivatives [39]. Poly(3-hexylthiophene) (P3HT) was used as a reference polymer. P3HT, poly(3-dodecylthiophene) (PDDT) and poly(3-methoxyethoxyethoxymethyl)thiophene (PMEEM) are PTh polymers with different side chains. P3HT, benzyl terminated P3HT (P3HT-benzyl), and bromoester terminated P3HT (P3HT-bromoester) are PTh with different end groups. Poly(3-hexylthiophene)-*b*-polystyrene (P3HT-*b*-PS), poly(3-hexylthiophene)-*b*-poly(butylacrylate) (P3HT-*b*-PBA), and poly(3-hexylthiophene)-*b*-poly(methylacrylate) (P3HT-*b*-PMA) are polythiophene-based block copolymers with different secondary polymer chains. And, poly(3-dodecylthiophene-*ran*-methylthiophene) (PDDTr-PMT) is a random copolymer with a different secondary polymer chain randomly inserted into the primary chain of PTh [44].

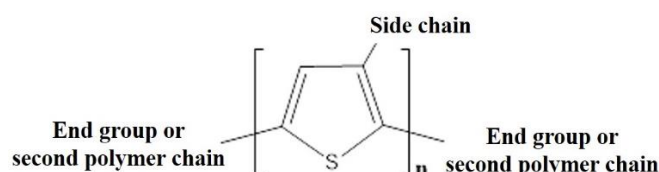
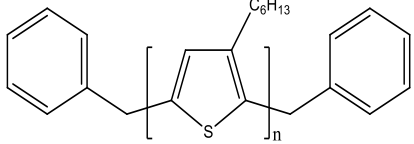
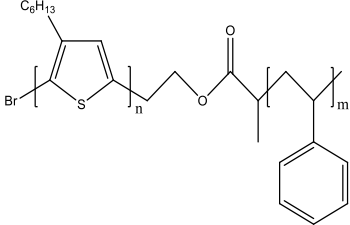
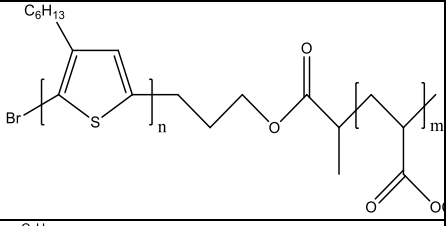
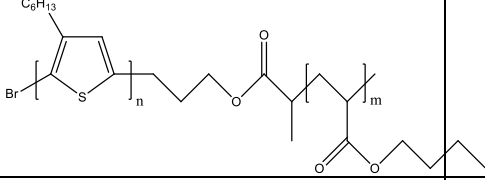
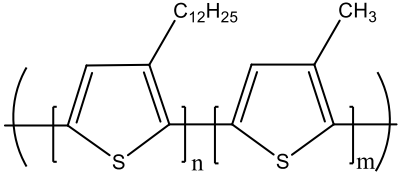


Fig. 2: Chemical structure of regioregular thiophene based polymers

According to Li et al. (2007) regioregular polythiophenes (rr-PThs) polymers have an air-stable conducting property that makes them suitable as chemiresistive sensing materials [39]. Their solubility in a variety of organic solvents also enables them to be inkjet-printed for device fabrication [45]. The backbone of the polymer is formed by thiophene rings and a chemical side-chain group can be attached on each thiophene ring along the polymer and an end-group or a secondary copolymer chain can be added to each end of the PTh chain. This variety of possible structures enables a potentially broadly applicable of candidate materials for volatile organic compounds (VOC) sensing. Combinatorial analysis of sensor arrays incorporating these multi-materials has the potential to provide strong and selective detection of VOCs via the 'electronic nose' concept [46].

Table 2: Chemical structures and properties of thiophene based polymers

PTh	Chemical structure	Composition ^a	Molecular weight ^b	Polydispersity index ^b
Poly(3-hexylthiophene) (P3HT)		100ml% P3HT	11600	1.2
Poly(3-dodecylthiophene) (PDDT)		100ml% PDDT	47352	1.2
Poly(3-methoxyethoxyethoxymethyl)thiophene (PMEEM)		100ml% PMEEM	N/A	N/A
Bromoester terminated poly(3-hexylthiophene) (P3HT-bromoester)		100ml% P3HT	11200	1.2

PTh	Chemical structure	Composition ^a	Molecular weight ^b	Polydispersity index ^b
Benzyl terminated Poly(3-hexylthiophene) (P3HT-benzyl)		100ml% P3HT	13670	1.2
Poly(3-hexylthiophene)- <i>b</i> -polystyrene (P3HT- <i>b</i> -PS)		65ml% P3HT	16500	1.3
Poly(3-hexylthiophene)- <i>b</i> -poly(methylacrylate) (P3HT- <i>b</i> -PMA)		80ml% P3HT	14620	1.2
Poly(hexylthiophene)- <i>b</i> -poly(butylacrylate) (P3HT- <i>b</i> -PBA)		82ml% P3HT	16000	1.2
Poly(3-dodecylthiophene)- <i>ran</i> -3-methylthiophene (PDDT- <i>r</i> -PMT)		50ml% P3HT	11950	1.2

^a Mole percentage of PHT composition was determined by ¹H NMR spectroscopy

^b Number average molecular weight and polydispersity were determined by GPC with polystyrene as standard

Functionalized the PTh has also attracted considerable interest owing to their interesting electrical, electrochemical and optical properties. The introduction of flexible pendant chains onto the backbone improves the solubility and processability allowing more complete characterization of the materials. For example, poly(3-alkylthiophene)s with large alkyl groups, such as butyl, can be readily melt- or solution-processed into films, which, after oxidation, can exhibit exceptionally high electrical conductivity [47]. Additionally, such introduction modifies the electronic properties of the polymer, thereby increasing the possibilities for industrial applications.

The PTh and its derivatives can be synthesized via electrochemical polymerization and chemical oxidation polymerization with corresponding monomers in various organic solvents, aqueous media or both. The generally accepted mechanism for the oxidative polymerization of thiophene involves the formation of radical cations. As an example the formation of PTh via chemical oxidation polymerization of thiophene using iron trichloride (FeCl₃) as an oxidant is shown in Fig. 3 [48]. FeCl₃ oxidative polymerization is more established in industrial applications, compared with the other two synthetic methodologies (metal-catalysed coupling reactions, electro polymerizations) owing to its relative simplicity of experimental setup and to higher monomer-to-polymer conversion [49].

The study on the polymerization of 3-hexylthiophene with FeCl₃ was carried out in aromatic solvents such as benzene, toluene, xylene, and mesitylene [50]. The result shows that the monomer conversion obviously rose up from 45 to 88 %, when the reaction temperature for the polymerization of 3-hexylthiophene by FeCl₃ in benzene was elevated from 6 to 23°C; the polymerization was accompanied by the formation of a large amount of cross-linked gel (from 0% at 6°C to 3 % at room temperature). The significant increase in the yield of acetone-soluble oligomers was found when polymerizations were carried

out at 23°C in toluene or xylene. These results may indicate the less reactivity of these tolyl and xylol terminated oligomers. Furthermore, the molecular weight of resultant P3TH synthesized in aromatic solvents was also affected by the reaction temperature where the polymerization of 3HT in CHCl_3 has been found to be larger as the molecular weight the polymerization temperature becomes higher. However, elevating the reaction temperature at the polymerizations of 3-hexylthiophene in aromatic solvents led to the formation of polymers with lower molecular weight and wide molecular weight distributions.

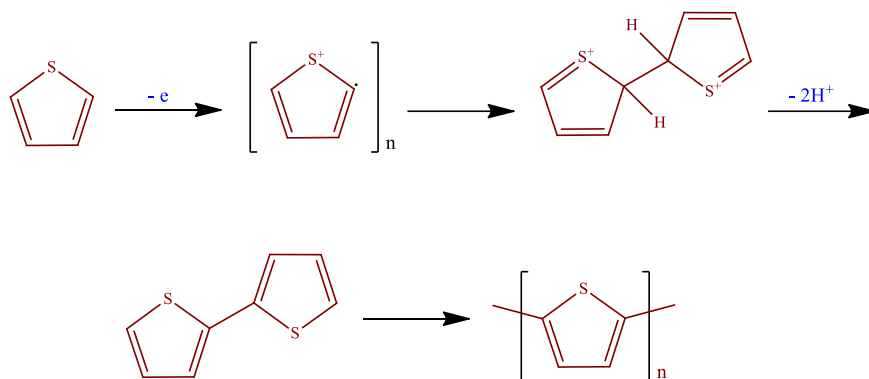


Fig 3: Formation of PTh via oxidation polymerization of thiophene monomer using FeCl_3

Chemical sensor characteristics

The principle of chemical sensor involves the transformation of the concentrations of analytes into the detectable physical signals, such as currents, absorbance, mass or acoustic variables. After exposing to the vapour of an analyte, the active sensing material of the sensor interacted with the analyte, which causes the physical property changes of the sensing material. The interactions between the analytes and the sensing materials are multiform, depending on the type of analytes and active materials [14]. The commercially available sensors were mostly based on metal oxides which mostly operated at high temperatures. However, the sensors made of conducting polymers have many enhanced characteristics for example high sensitivities and short response time; especially, these features are ensured at room temperature.

Many important organic analytes, such as benzene (C_6H_6), toluene (C_7H_8), and some other volatile organic compounds (VOCs) are not reactive at room temperature or under mild conditions. Therefore, it is difficult to detect them by their chemical reactions with conducting polymers. However, detection by physical interaction with conducting polymer is feasible. This interaction involves adsorbing or swelling of the polymer matrixes that may influence the properties of the sensing materials and therefore make these gases detectable. Adsorbing of the analyte molecules on the surface of the sensing conductive film is widely used in gas sensing. Indeed, the adsorption is the first step in all the sensing techniques, especially in same quartz crystal microbalance sensors [51].

Whereas, swelling of the polymer film is an important mechanism to interpret sensing behaviour of conducting polymer to organic vapours [52]. Like other polymers, conducting polymers can swell in many organic solvents, and this has been detected by atomic force microscope (AFM) [53]. The swelling behaviour is controlled by the vapour molecular volume, the affinity of the vapour to the sensing polymer and the physical state of the polymer [54]. At ambient temperature, most conductive polymers are in their glassy state, thus some researchers pointed out that a low sorption and swelling level are expected and their contribution to the overall electrical resistance decrease is lower [55]. Whereas, for a pure conductive polymer, inserting analyte molecule into polymer matrix generically increases interchain distance, which affects the electron hopping between different polymer chains. Hydrogen bonding and dipole-dipole interactions are also reported to play important roles for the gas detection in sensor response.

The primary charge carrier and the type of gas interacting with the active layer induce the change of sensor's resistance upon the gas exposure. From the viewpoint on practical application, a sensor should present rather high selectivity because a high response usually enhances the detection limit, whereas a better selectivity usually enables the gas sensor to exclusively response to a certain target gas. Thus, selectivity is important gas-sensing performance character for sensing materials. The mechanism of chemical sensing for the analyte detection are shown in Fig. 4. Although several compiled sensors make up

a p-n heterojunction, they are decidedly sorted into their single dominant charge carrier trait of either n-type or p-type behaviour based on how resistivity decreases or increases in the augmentations of analyte concentration. This is to guarantee a straightforward understanding and an effective assessment of analyte sensing characteristics for both n-type and p-type gas sensors. The sensing response of p-type graphene based chemical sensor over the chemical or analytes detection was determined using Eqn. 1.

$$S (\%) = \Delta R/R_g \times 100 = (R_g - R_o)/R_o \times 100 \quad (1)$$

Where R_o and R_g are the electrical resistance of graphene based sensor before and after the exposure to analytes (e.g. NH_3) at specific time, temperatures etc., respectively.

Table 3: Sensing response behaviour of p-type and n-type sensors to reducing and oxidizing analytes

Sensing response behaviour	Examples of analytes	p-type sensor	n-type sensor
Reducing analytes	CO, NH_3 , $\text{C}_2\text{H}_5\text{OH}$, etc.	Resistance increases	Resistance decreases
Oxidizing analytes	NO, NO_2 , O_3 , etc.	Resistance decreases	Resistance increases
Dominant charge carrier	-	Holes (h^+)	Electrons (e^-)

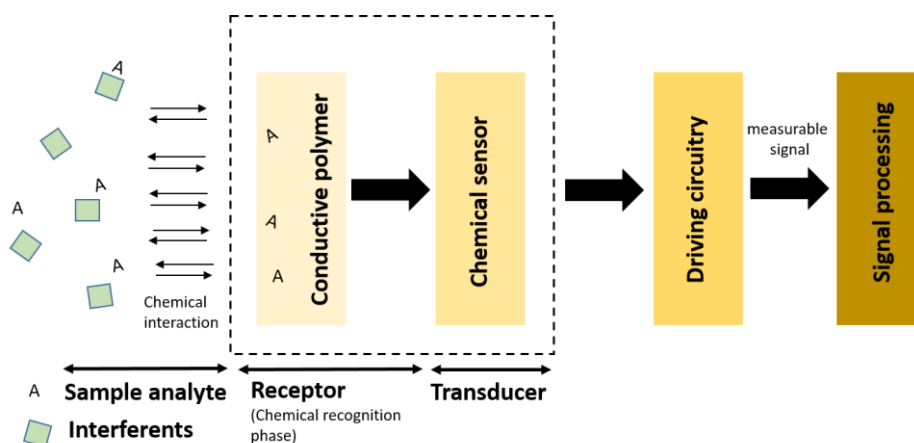


Fig. 4: Schematic diagram of chemical sensing mechanism

Development of polythiophene in chemical sensor

The used of conductive polymers, such as PPy, PANI, PTh as an active layers of gas sensors since early 1980s [56]. Organic polymers are one of the principal materials applied in gas sensing systems. Some conducting polymers can behave like semiconductors due to their heterocyclic compounds which display physicochemical characteristics. As a result, reversible changes in the sensing layer's conductivity can be detected upon polar chemicals' adsorption on the surfaces at room temperature [57]). This effect is believed to be caused by the charge transfer between gas molecules and the polymer or the polymer film's swelling [58]. PTh and its derivatives such as P3HT, poly(3-alkylthiophenes) (P3AT), and poly(3-octylthiophene) (P3OT) etc. are well-known studied polymers for photoelectronic applications due to its relative stability in air and processability in solvents, their p-type semiconducting behaviour and optical band gap of around 2eV [59-60]. In this section, the research progress on PTh nanocomposites with graphene, carbon nanotubes and metal oxides has been reviewed.

Polythiophene with graphene

Study by Bai et. al. (2016) on the enhancement of NO_2 sensing performance at room temperature by graphene-modified PTh [61]. The results found that the 5% reduced graphene oxide-PTh (rGO-PTh) sensor not only has much higher response to NO_2 but also exhibits higher selectivity to NO_2 than to the mentioned gases with a fixed concentration, 10ppm (Fig. 5). Thus, the 5% rGO-PTh hybrid is a promising sensing material for efficient and selective detection of NO_2 [62].

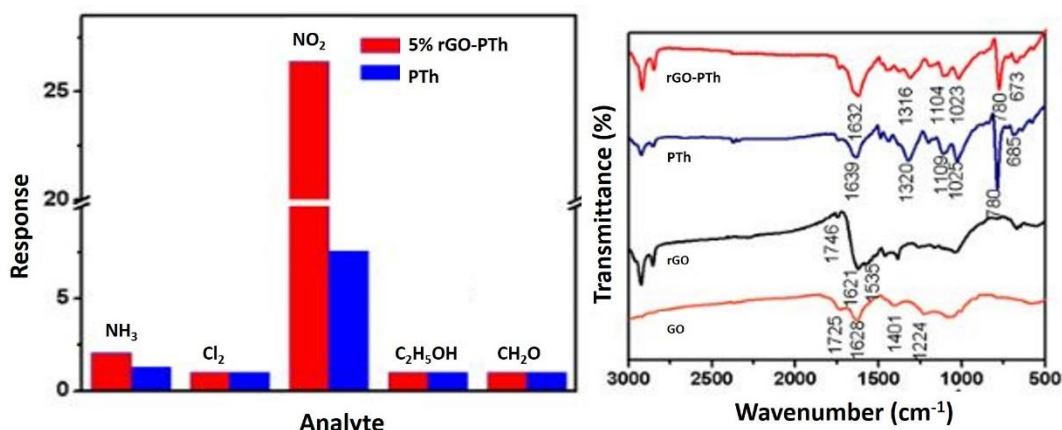


Fig. 5: Response of tested analyte on sensors based on PTh, 5% rGO-PTh at room temperature and the FTIR spectroscopy of rGO-PTh

According to Bai et al. (2015), there are three possible reasons for the excellent sensing performance of their rGO-PTh hybrid samples [63]: (1) The sensing principal of such sensor involves adsorption/desorption on surface of material. A larger surface area of hybrid is can be achieved by incorporating rGO, which is beneficial to improve the sensing performance [63-64]; (2) PTh can interact with rGO through π - π interaction. FTIR analysis confirms that π - π interaction exists between the PTh and rGO, and this π - π interaction had caused a charge carrier increase, and the electron transfer may occur between the conjugated PTh and rGO sheets, which results in the resistance decrease of hybrids. Additionally, the introduction of RGO could also improve the electron-transfer rate during the process of NO₂ sensing; (3) Referring to the FTIR analysis (Fig. 12), the characteristic peak located at 1639cm⁻¹ of PTh is shifted to 1632cm⁻¹, which means that the required energy of electrons to delocalize along the PTh chain comparatively decreases. This suggests that NO₂ will capture electrons from hybrids more easily. Therefore, the resistance of hybrid in NO₂ decreases, finally increasing the sensing performance of the resultant hybrid [65-66].

Another study for the detection of OPs, methyl parathion is through the study by Ramachandran and Dhayabaran (2019) on the utilization of a MnO₂/PTh/rGO nanocomposite modified glassy carbon electrode as an ultrasensitive electrochemical sensor for detection methyl parathion (MP) [67]. The sensor displayed excellent performance over a wide linear range of MP (0.5 to 10 μ l) with a detection limit of 5.72nM. In real samples (human urine and serum), the limit of detection (LOD) was determined to be 1.3nM in blood and 4.8nM in urine. The sensitivity was about 0.0498 and 2.6099 for blood and urine samples, respectively. The corresponding results are shown in Table 3. The developed sensor exhibited excellent performance for determination of MP in human serum and urine samples. The results indicated that the sensor could be practically applied for the detection of MP in human samples.

Table 4: The percentage of recovery on determination of MP in real samples using MnO₂/PTh/rGO/GCE

Real sample	Amount of MP added/ μ M	Found/ μ M	Recovery %	RSD %
Blood serum sample	0.5	0.46	92.2	2.04
	1	0.93	93.9	
	3	2.87	95.9	
	5	4.70	94.1	
	10	9.72	97.2	
Urine sample	0.5	0.47	94.9	3.5
	1	0.96	96.8	
	3	2.81	93.3	
	5	4.10	89.9	
	10	8.42	88.5	

P3HT/graphene nanocomposite based field-effect transistor was fabricated, characterized and further used for the application of NH₃ gas detection. Graphene as nanofillers in polymer matrix may

provide large surface area for adsorbents and interactions with gas molecules, so, graphene act as an excellent gas sensing candidate applicable in organic sensor devices. Here, fabricated P3HT/graphene active channel based field-effect transistors (FETs) were placed in NH_3 gas environment for a range of concentrations (0.25 to 25 ppm) to discover this device as sensor, at room temperature. Device key performances parameters like drain current, threshold voltage and mobility in absence and presence of NH_3 was examined. It was found that the device key parameters (calculated in absence of NH_3) were changed significantly as device was exposed into various concentrations of the NH_3 gas. The structural morphology of the developed nanocomposite was also studied under scanning electron microscope. The P3HT/graphene nanocomposite based OFET demonstrated excellent sensitivity of NH_3 at room temperature with better reversibility and reproducibility in comparison to alone polymers (P3HT) based devices [68].

Hybrids of ethylenediamine modified-rGO and PTh were synthesized successfully by in-situ chemical polymerization under room temperature for 2 h and loaded on a flexible PET film to construct a smart sensor. The sensing performance of pure PTh and hybrids based sensors to NO_2 was examined at room temperature. The results of the hybrid film sensor with 5 wt.% rGO not only exhibits high sensitivity to 10 ppm NO_2 gas, which is nearly 4 times higher than that of pure PTh, and excellent selectivity, but also has flexible, low cost, portable and wearable characteristics. The mechanism of sensing performance enhanced by incorporating graphene into PTh also was discussed, which is attributed to large specific surface of the hybrid and synergetic effects between the components in hybrid [61].

Graphene/PTh has been also introduced as an effective material to prepare flexible gas sensors for the detection of various chemicals such as NO_2 , NH_3 , H_2 , H_2S , CO_2 , SO_2 , ions including Cd, Hg, Pb, Cr, Fe, Ni, Co, Cu, Ag, and volatile organic compounds comprising nitrobenzene, toluene, acetone, formaldehyde, amines, phenols, bisphenol A, chemical warfare agents, and environmental pollutants. This is mainly due to the oxygenated functional groups in graphene oxide (GO) imparting amphiphilic property, which facilitates the reactivity toward different types of molecules on the graphene surface. A change in electrical resistance of graphene occurred through formation of a charge-transfer complex by interaction with chemical target acting as electron donor or acceptor [61, 69-70].

PTh/graphene nanocomposite for ethanol detection has been investigated by [71]. The result shows that a uniform lamination of PTh on graphene nanosheets shows an excellent sensitivity compared to pristine PTh. This leading to a considerably low detection limit of 400 ppm and complete reversibility within 360 s at room temperature. Significantly, PTh/G-3 (15% graphene) was observed to be excellent in selectivity towards ethanol than various volatile hydrocarbons tested. The sensing mechanism was presented citing the involvement of polarons of PTh and lone pairs of electrons of ethanol during adsorption and desorption on the surface of PTh/G-3 is responsible for the variation in direct current (DC) electrical conductivity (Fig. 6). As depicted in Fig. 6 (c), the presence of ethanol molecules is adsorbed on the surface of PTh/G-3 nanocomposites and the lone pairs of electrons on the oxygen atom of ethanol molecule interact with polarons of PTh in PTh/G-3 nanocomposites which impede the mobility of polarons which automatically reduce the electrical conductivity. In the presence of ambient air, ethanol molecules get desorbed from the surface of PTh/G-3 nanocomposites. Thus electrical conductivity reverted to its original value. The simple adsorption-desorption process of ethanol on the large surface area of PTh/G-3 nanocomposites significantly affect the mobility of polarons which is responsible for the decrease and increase in electrical conductivity when exposed to ethanol and the ambient air respectively [71].

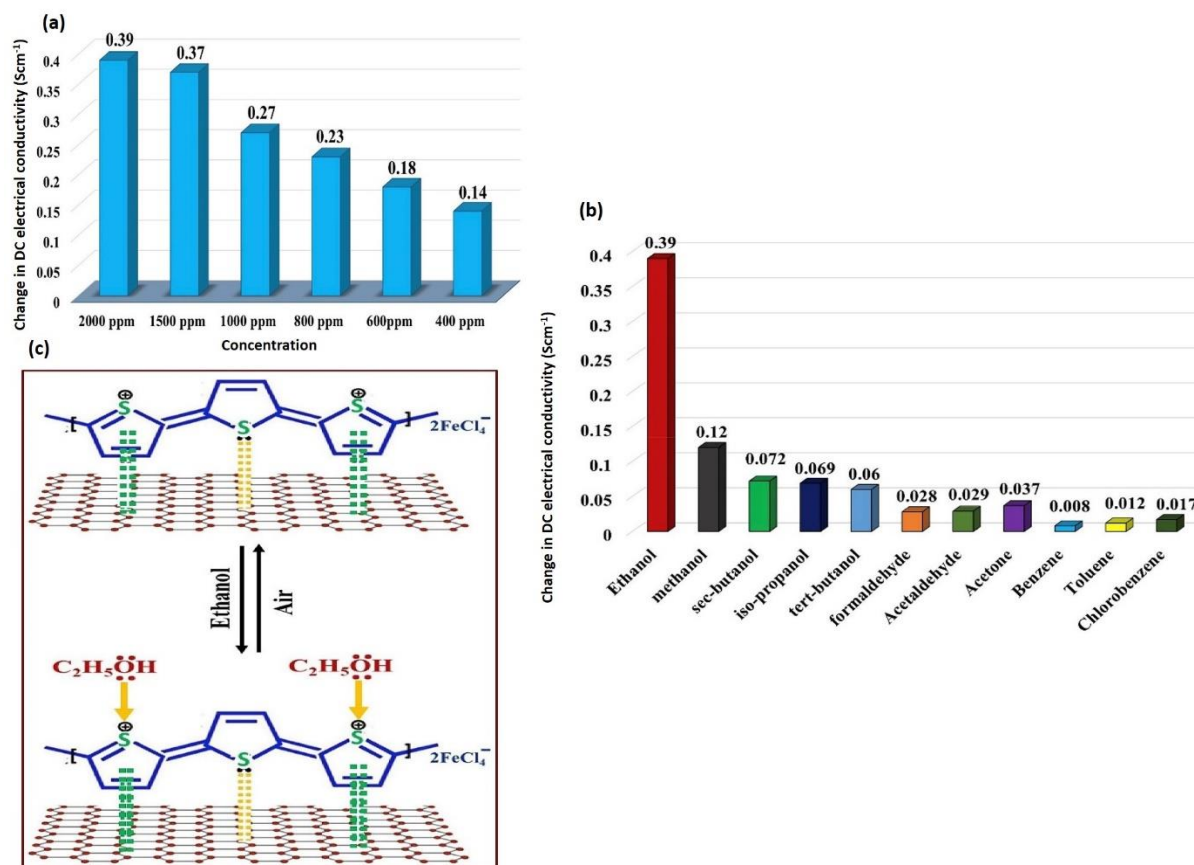


Fig. 6: (a) Change in conductivity of PTh/G-3 on exposure to different concentrations of ethanol at 60 s, (b) selectivity of the PTh/G-3 towards ethanol and different VOCs on exposure to 2000 ppm for 60 s and (c) sensing mechanism of interaction of ethanol with PTh/G-3 nanocomposite [71]

Sensing mechanism of polythiophene/graphene

Sensing response of the samples as a function of variation in DC electrical conductivity of PTh and PTh hybrid with graphene nanosheets towards ethanol is centred on the reduction in DC electrical conductivity on exposure to ethanol and revert to the original value when exposed to the ambient air. In PTh/G-3 (graphene 15% wt.%) nanocomposite, π -electrons of graphene nanosheets interact with lone pair on the sulphur atoms of PTh. Thus, hopping of charge carriers from PTh to graphene nanosheets achieve rapid movability along with the extended π -conjugated system of graphene nanosheets resulting in the improvement in electrical conductivity of PTh/G-3. The sensing mechanism of the PTh/G-3 nanocomposites was described on the basis of DC electrical conductivity response through a simple adsorption-desorption mechanism of ethanol at ambient temperature (27°C). In the presence of ethanol, ethanol molecules are adsorbed on the surface of PTh/G-3 nanocomposites and the lone pairs of electrons on the oxygen atom of ethanol molecule interact with polarons of PTh in PTh/G-3 nanocomposites which impede the mobility of polarons which automatically reduce the electrical conductivity. In the presence of ambient air, ethanol molecules get desorbed from the surface of PTh/G-3 nanocomposites, therefore, electrical conductivity reverted to its original value. Hence, the simple adsorption-desorption process of ethanol on the large surface area of PTh/G-3 nanocomposites significantly affect the mobility of polarons which is responsible for the decrease and increase in electrical conductivity when exposed to ethanol and the ambient air, respectively [71].

Polythiophene with carbon nanotubes

Theoretically, the carbon atoms in a carbon nanotube are surface atoms, which makes them optimally suited for components of chemical sensors. Hence, it is not surprising that gas sensors made from individual nanotubes show good sensitivity and exhibit fast response and substantially higher sensitivity than that of existing solid-state sensors at room temperature upon the exposure to gaseous molecules such as NO₂ or

NH₃ [72-73], in comparison to commercially available classical semiconductor sensors, which in general operate above 200°C. However, a necessary prerequisite is that the molecules to be detected must have a distinct electron donating or accepting ability, for example, NH₃ as a donor and NO₂ as an acceptor.

It has been reported that CNTs are very sensitive to the surrounding environment. The presence of O₂, NH₃, NO₂ and dimethyl methylphosphonate (DMMP) gases and many other molecules can either donate or accept electrons, resulting in an alteration of the overall conductivity [74-76]. This is because the adsorption of these molecules on the nanotubes is associated with a partial charge transfer, which alters the charge-carrier concentration, or alternatively, the adsorbed molecules may affect the potential barriers present at the tube-electrode contacts. In any circumstance, the resulting change in the electrical resistance of the individual nanotube is utilised as a sensor signal. However, for the detection of molecules that are only weakly adsorbed (e.g. CO and H₂), the change in resistance is often too small. A possible method to overcome this drawback is by the functionalisation of the side wall of CNT with a conductive polymer [77].

Since the most common gas sensing principle is the adsorption and desorption of gas molecules on sensing materials, it is quite understandable that by increasing the contact interfaces between the analytes and sensing materials, the sensitivity can be significantly enhanced. Recent development in nanotechnology has created huge potential to build highly sensitive, low cost, portable sensors with low power consumption. The extremely high surface-to-volume ratio and hollow structure of nanomaterials is ideal for adsorption and storage of gas molecules. Therefore, gas sensors based on nanomaterials with conductive polymer, such as CNTs, nanowires, nanofibers, and nanoparticles, have been investigated widely [78-84].

Chemiresistors based on hexafluoroisopropanol substituted polythiophene/single wall carbon nanotubes (HFIP-PTh/SWCNT) hybrid system were shown to be highly sensitive and selective for DMMP [85]. It was found that the sensor response is fast and reproducible even at low analyte concentrations. At equilibrium vapour pressures of DMMP, the HFIP-PTh/SWCNT sensor has about 40% larger response than the P3HT/SWCNT. Whereas at 1ppm, the DMMP HFIP/SWCNT is 9 times more sensitive. As such, it gives an 8% conductance change upon exposure to 0.6ppm of DMMP. Moreover, the H-bonding ability of HFIP-PTh/SWCNTs has greatly increased the response and selectivity for DMMP, as compared to P3HT/SWCNTs and SWCNTs. The enhancement due to the HFIP-PT is most impressive at low analyte concentrations. Fig. 7 shows the conductance change and the sensitivity of the SWCNT sensors in response to common organic solvents and DMMP diluted to 1% of saturated vapour conditions at room temperature, with a fixed voltage at 0.1 V [85].

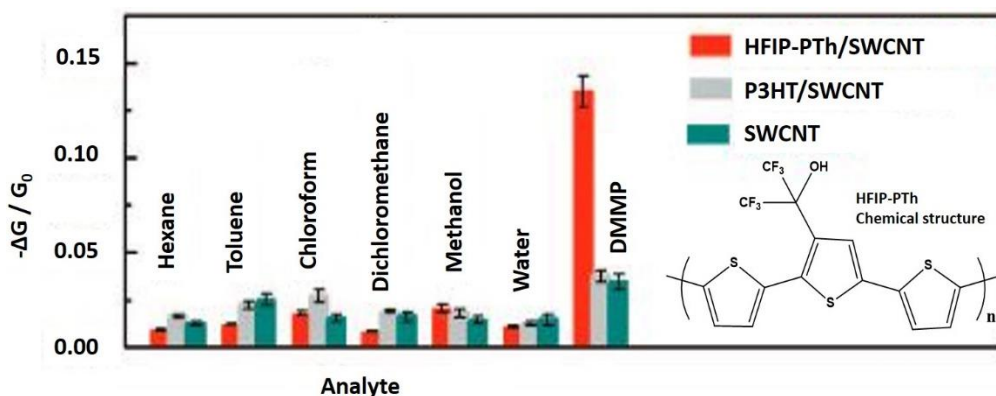


Fig. 7: Conductance and sensitivity of the HFIP-PTh/SWCNT, P3HT/SWCNT and SWCNT sensors in response to common organic solvents and DMMP

In term of organophosphates study (OPs), a study of nanocomposite consisting of PEDOT and -COOH functionalized multiwalled carbon nanotubes (MWCNTs) has been used for the analysis of malathion organophosphate on the spiked lettuce bought from a local supermarket [86]. It was inferred that the AChE (acetylcholinesterase)/PEDOT-MWCNTs/FTO bioelectrode exhibits reasonably a good recovery of about 96 to 98%. The reason for less than 100% recoveries is that the standard malathion solution is a pure compound with no impurities. The lettuce sample bought from a local supermarket might contain some of the interfering compounds that interacted with the enzyme non-covalently and blocked the active sites. This may lead to the less availability of the active sites for interaction with malathion that results to less than 100% recoveries. In case of spiked sample, the AChE/PEDOT-MWCNTs/FTO bioelectrode retained

98% and 83% activity up to the first and fifth use of a single bioelectrode respectively, thereby, confirming a good reproducibility of the enzymatic bioelectrode by 2-pyridine aldoxime methiodide (2-PAM).

A vapor phase chemical sensor with a viewing area of 0.78 mm^2 (diameter 1 mm) is constructed using a novel nanocomposite material made up of multiwalled carbon nanotubes (MWCNT) and poly (3-methylthiophene) that shows a change in electrical resistance upon exposure to different chloromethanes. The resistance change is proportional to the concentration of the analyte. The sensor does not respond to methane, acetone, acetaldehyde, benzaldehyde, tetrahydrofuran, methanol and ethanol. The nanocomposite is characterized by well-defined transitions in Fourier transform infrared spectroscopy and thermogravimetric analysis. The response time of the sensor is generally about 60–120 s. The sensor is capable of selectivity to any mixture made up of chloromethane and methane. The mechanism of sensing of chloromethane is discussed [87].

Sharma et al. (2014) reported on PEDOT: PSS and PANI on MWCNTs, which were compared for their NH_3 gas-sensing performance at room temperature, and the DC electric field and heating-cooling profile were controlled to optimize fast and complete recovery [88]. Both sensors exhibited excellent sensitivity. However, upon comparison, the MWCNT/PEDOT:PSS composite was revealed to be considerably more sensitive ($\sim 16\%$ better sensitivity) with a shorter response time ($\sim 15 \text{ min}$). Furthermore, the thermal stability of the MWCNT/PEDOT: PSS composite appeared to be much better than that of the MWCNT/PANI composite and showed excellent repeatability of standard resistance in the optimized recovery condition [88].

Poly (3,4-ethylenedioxythiophene) doped with poly (styrene sulfonic acid) (PEDOT: PSS) coated single walled carbon nanotubes (SWNTs) sensors had been fabricated and studied for detecting analytes of interest in industrial manufacturing. By varying the conducting polymers synthesis conditions in terms of charge controlled electropolymerization of the monomer EDOT in presence of the dopant PSS, the sensing performance of the PEDOT:PSS functionalized SWNT sensors was systematically optimized. Electrical characterization in terms of change in resistance, cyclic voltammetry and field-effect transistor measurements was performed to confirm the presence of PEDOT:PSS coating on SWNTs. The optimized sensors exhibited sensing properties over a wide dynamic range of concentrations towards saturated vapours of volatile organic compounds (VOCs) such as methanol, ethanol and methyl ethyl ketone (MEK) at room temperature. The limit of detection of this sensor was found to be 1.3%, 5.95% and 3% for saturated vapours of methanol, ethanol and methyl ethyl ketone (MEK) respectively. In terms of performance, when compared with bare SWNTs, these hybrid sensors exhibited better sensitivity. The underlying mechanism of sensing was also investigated by using them in chemFET mode of sensor configuration [89].

Sensing mechanism of polythiophene/carbon nanotubes

Referring to Husain et al. (2020) in their study on ultra-sensitive, highly selective and completely reversible NH_3 sensor based on PTh/SWCNT nanocomposite, the lone pairs of PTh interact with π -electrons of SWCNT [71]. As a result, hopping of polarons (charge carriers) takes place from PTh to SWCNT where they attain abrupt transferability along with the extended π -conjugated structure of SWCNT, which causes the electrical conductivity of PTh/SWCNT-3 to rise significantly. The decrease and increase of DC electrical conductivity by the simple adsorption-desorption of NH_3 vapours at room temperature (27°C) was the basis of explaining the sensing mechanism of PTh/SWCNT as presented. On exposure to NH_3 , the lone pairs of NH_3 impede the mobility of polarons of PTh/SWCNT nanocomposite, resulting in a decline in the DC electrical conductivity. Once exposed in the ambient air, NH_3 molecules desorbed from PTh/SWCNT, and thus the DC electrical conductivity reverted to its original value. The mobility of polarons which causes loss and regain of DC electrical conductivity is considerably governed by the adsorption-desorption route of NH_3 molecules on the vast surface of PTh/SWCNT [90].

Polythiophene with metal oxide

Semiconductor metal oxide are the most commonly used materials for the fabrication of chemical sensors due to their versatile properties. Nowadays, much research has been focused on hybridising an inorganic semiconductor metal oxide with organic conducting polymer to form a hybrid material with enhanced performance as compare to their individual counterparts. Such nanocomposites have demonstrated their

advantage in various applications like chemical sensors, solar cells and organic electronics etc. [91-92]. Metal oxide nanostructures are favourite candidate for the development of sensors as they possess remarkable characteristics like chemical stability, easy to fabricate, controllable size, excellent catalytic properties and facilitated electron transfer kinetics. Thus, metal oxides such as zinc oxide (ZnO), Titanium oxide (TiO_2), Tin(IV) oxide (SnO_2), tungsten trioxide (WO_3), iron (III) oxide (Fe_2O_3) etc. have been widely exploited for the development of electrochemical sensors for the detection of harmful pollutants and gases.

Based on the sensing mechanism of conductive polymer with metal oxide, like SnO_2 or TiO_2 proposed by Ram et al. (2005), this can be one of the most interesting nanostructured material for gas sensing application [93]. This is because of an excellent change in conductivity at room temperature possesses excellent optical and catalytic properties. Fig. 8(a) shows a model of gas reaction of conductive polymer- SnO_2 nanocomposite device to the exposure to NO_2 -concentration. The n-type SnO_2 forms a hetero p-n-junction to conducting polymer p-type channel with a depletion region. The device resembles a field effect transistor (FET). The gas effects a change of the depletion region and thus modulates the conductivity of the junction. Exposure to NO_2 causes a depletion of the SnO_2 carrier concentration. Less carriers in the SnO_2 layer causes a reduction of the channel electric field of the junction. The width of the depletion region decreases and the conductivity of the thiophene channel increases. NO_2 exposure causes an increase in E_c - E_F in the n-region, involving the reduction of the width of the depletion region. In addition, the resistance of conductive polymer like PTh decreases continuously and exponentially upon exposure to NO_2 , indicating that the gas acts as a dopant for the polymer (Fig. 8 (b)) [93].

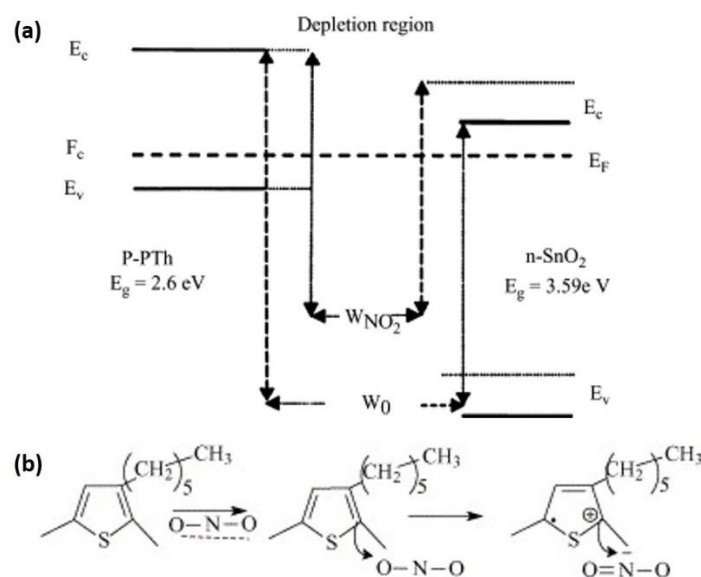


Fig 8: Energy-band of hetero p-n-junction (dashed lines show energy levels under NO_2 exposure) and (b) schematic of the NO_2 reaction with P3HT conductive polymer

An electrochemical approach was developed for rapid and effective detection of hydrazine using PTh/ ZnO nanocomposite modified glassy carbon electrode (GCE) [94]. Cyclic voltammetry measurements using the PTh/ ZnO modified GCEs revealed remarkable sensing response toward hydrazine compared to either bare GCE or pure ZnO , with diffusion-controlled electrode kinetics. The limit of detection (LOD) calculated from the electrochemical measurements was found to be $0.207 \mu\text{M}$ at ($S/N = 3$). Most significantly, the PTh/ ZnO modified electrodes showed good operational stability, repeatability and reproducibility and allowed sensitive detection of hydrazine in the presence of several common interfering molecules.

Bai et al. (2014) have synthesized PTh/ WO_3 hybrid structures for the detection of H_2S . the prepared PTh/ WO_3 nanocomposites exhibited excellent response, good selectivity and fast recovery of H_2S at temperature of 70°C [95]. Furthermore, Ram et al. (2005) had designed PTh/ SnO_2 and poly (ethylenedioxythiophene) (PEDT)/ SnO_2 based sensor showing excellent sensitivity for the detection of NO_2 at ppb levels [93]. Ma et al. (2006) have reported that the PTh film showed gas response to trimethylamine, ammonia, alcohol, acetone, and toluene at room temperature [96]. However, poor selectivity is the most serious problem for inorganic and organic conducting polymer sensing material. The nanocomposites of

PTh and tin dioxide (SnO_2) was synthesized in situ chemical oxidative polymerization method where it has been used for gas sensing to methanol (MeOH), ethanol (EtOH), acetone, and NO_x at different working temperature [97]. It was found that PTh/ SnO_2 materials with different PTh mass percent (1%, 5%, 10%, 20% and 30%) could detect NO_x with very higher selectivity and sensitivity at much lower working temperature than the reported SnO_2 . Among all of the PTh/ SnO_2 composites, PTh (5%)/ SnO_2 showed the highest sensitivity at room temperature. The possible mechanism of the composites has been suggested to be the formation of p-n heterojunction. However, it was found that PTh/ SnO_2 composites with different PTh mass percent could exhibit high sensitivity to NO_x , but no sensitivity to 10 ppm, 50 ppm, 100 ppm, 150 ppm and 200 ppm MeOH , acetone, and EtOH . Referring to the authors, such materials offer excellent properties at room temperature, which suggest the potential application of the PTh/ SnO_2 composites in gas sensor field.

The sensing properties of molecular composites, tetratertbutyl copper phthalocyanine (TBCPC) and polyoctadecyl thiophene (PODT), were investigated by optical and conductance measurements. A standard substrate for gas sensing was made, consisting of a set of eight interdigitated gold electrodes, 230 μm wide and spaced, and 0.10 μm thick, photo-lithographically fixed on an SiO_2 coated silicon wafer. Langmuir-Blodgett (LB) films of different thickness and composite compositions were fabricated at different surface pressures. The gas sensing behavior of the films, on exposure to NO_2 and NH_3 gases, depends on the mutual ratio of components of the composite. The film thickness determines the response speed on exposure to gases and their reversal. It was also found that the films deposited at lower surface pressures show larger and faster response and better recovery kinetics. The electrical properties of gold contacts to these LB layers were evaluated by current-voltage characteristics, which are linear over the whole measuring range. Very short response times, reasonably good reproducibility, and fair composition dependent sensitivity at room temperature make this molecular composite a very promising candidate for neuron network sensing elements [98].

In brief, PTh does play a good role in development of chemical sensors. The adsorption of organic gases and swelling process on conducting polymers used in development of gas sensing. Next, the chemical sensors transform the aforementioned analytes into signals that could be detected, such as currents, resistances, absorbance, mass or acoustic variables. In addition, PTh-based sensor has quite higher sensitivity compared to other conductive polymers that already well-commercialized, and this will be a good turning point for PTh sensor as competitive chemical sensors.

Xu et al. (2010) reported SnO_2 hollow sphere/PTh hybrid materials that were fabricated by an in situ chemical oxidative polymerization method [99]. The SnO_2 hollow sphere/PTh hybrids demonstrated a powerful synergistic interaction between the SnO_2 hollow sphere and PTh, and the hybrids had higher thermal stability than pure PTh, showing high selectivity, good response, and a comparatively short recovery time to NO_2 gas at 90°C . The enhanced gas performance was due to the high surface area of the hybrids and the p-n heterojunction arranged between p-type PTh and n-type SnO_2 hollow spheres [99].

Guo et al. (2012) prepared PTh/nanosized WO_3 organic-inorganic hybrids fabricated by a chemical oxidative polymerization and colloidal chemical method [100]. The PTh/ WO_3 hybrids with different mass fractions of PTh were acquired by mechanically mixing the prepared PTh and WO_3 . The hybrid composite exhibited higher response for NO_2 sensing below 90°C than pure PTh and WO_3 sensors. The response of the PTh/ WO_3 hybrids was influenced by the PTh mass fraction. The 20 wt.% PTh/ WO_3 hybrid demonstrated high response and good selectivity to NO_2 gas below 90°C [100].

A highly conductive polythiophene films with electrical conductivity of 71.7 Scm^{-1} were prepared by using a facile solution-processing method with HAuCl_4 as a dopant. The density of free charge carriers for thus-prepared polythiophene films was estimated to be $4.48 \times 10^{21}/\text{cm}^3$. In addition, upon doping, the color of the polymer films changed significantly with the main absorption peaks bathochromically shifted from the visible to near-infrared region. Interestingly, the polythiophene films could be easily dedoped when exposed to organic amines and thiols. The dual variations of film color and electrical conductivity thus were exploited for the design and fabrication of a logic circuit, in combination with polythiophene films doped by electrochemical oxidation, for selective detection of volatile amines and thiols with a detection limit lower than 1 ppm. The results demonstrate the high potential of this solution-doping method in the preparation of highly conducting organic thin films for vapor sensing [101].

An approach was proposed to evaluate the performance of organic thin film transistors (OTFTs) gas sensors. Back-gated OTFTs gas sensors with P3HT/ZnO nanorods composite film as the active layers and gas sensing layers were prepared for NO₂ detection. Response characteristics of gas sensors to NO₂ were studied. It can be found that responses of OTFTs gas sensors were inaccurate according to conventional definition. The slope of fitting line was proposed as a new method to evaluation gas properties of OTFTs sensors. The calculate results the sensitivity can be increased up to 40.2% due to appropriate amount of ZnO-nanorods doping [102].

A dramatic visible light photoelectrochemical sensing platform for the detection of pesticide molecules at zero potential (versus saturated calomel electrode) was first constructed using P3HT functionalized with TiO₂ nanoparticles. The P3HT was synthesized via chemical oxidative polymerization with anhydrous FeCl₃ as the oxidant, 3-hexylthiophene as the monomer, and chloroform as the solvent, and the functional TiO₂ nanoparticles were facily prepared by blending TiO₂ nanoparticles and P3HT in chloroform solution. Under visible light irradiation, P3HT generated the transition from the valence band to the conduction band, delivering the excited electrons into the conduction band of TiO₂ and then to the glassy carbon electrode. Simultaneously, a positive charged hole (H⁺) of TiO₂ may form and migrate to the valence band of P3HT, which can react with H₂O to generate •OH, and then it converted chlpyrifos into chlpyrifos• that promoted the amplifying photocurrent response. On the basis of the proposed photoelectrochemical mechanism, a methodology for sensitive photoelectrochemical sensing for chlpyrifos at zero potential was thus developed. Under optimal conditions, the proposed photoelectrochemical method could detect chlpyrifos ranging from 0.2 to 16 μmol L⁻¹ with a detection limit of 0.01 μmol L⁻¹ at a signal-to-noise ratio of 3. The photoelectrochemical sensor had an excellent specificity against the other pesticides and could be successfully applied to the detection of reduced chlpyrifos in green vegetables, showing a promising application in photoelectrochemical sensing [103].

PTh nanocomposite with nanofibers, with 70 to 150 nm in diameter, containing ZnO nanoparticles were synthesized through a self-assembly process in the presence of hexadecyltrimethylammonium bromide (CTAB) as the surfactant. Gas-sensing properties of the prepared sample have been investigated for different concentrations of NH₃ gas at room temperature. A template-like model was proposed to interpret the formation of the composite nanofibers. Gas sensing tests showed that the chemiresistor based on the as-prepared hybrid has high sensitivity, excellent repeatability, long-term stability and short response time to NH₃ gas at room temperature. Therefore, the ZnO/PTh hybrid can be expected to be potentially used as a gas sensor material for detection of NH₃ gas at room temperature. The sensing mechanism of ZnO/PTh nanocomposite to NH₃ gas was presumed to be the effect of p-n heterojunction between ZnO nanoparticles and PTh [104].

Sensing mechanism of polythiophene/metal oxide

Referring to Xu et al. (2010), there are two possible reasons responsible for the excellent sensing performance of the PTh/hollow sphere SnO₂ (hs-SnO₂) nanocomposite, including good gas response, selectivity and comparatively short recovery time to NO₂ at low temperature [99]. On the one hand, the surface areas of the pure PTh and the (40%)PTh/hs-SnO₂ hybrids are 16 m²/g and 40 m²/g, respectively. It is obvious that, compared with the hs-SnO₂ (42 m²/g), the PTh adding does not induce remarkable effect on the surface area of the hybrids, especially containing 40 wt.% PTh, that is, the maximum PTh content by calculation. Therefore, it is adequately proved that the PTh/hs-SnO₂ hybrids have higher surface to volume ratio because of the loose and porous structure of hs-SnO₂, which can improve the gas diffusion process, therefore benefiting the gas sensor response and especially shortening recovery-response time. The p-n heterojunctions are expected to be formed between the p-type PTh and n-type hs-SnO₂, which could generate a unique electron donor-acceptor system, increasing the depletion barrier height, and thus improving the response and recovery of the sensor. The test gas can adjust the conductivity of the junction by changing the depletion region. When the gas NO₂ was introduced, the width of the depletion region decreased and the conductivity of the PTh channel increased. Hence, the PTh/hs-SnO₂ shows much higher response and fast response-recovery time in comparison to pure PTh. However, when compared with pure n-type SnO₂, the response of the hybrids is lower. For example, when the concentration of NO₂ gas is 10 ppm, the value of gas response is 143, while 2.07 for the (20%) PTh/hs-SnO₂ hybrids at 90°C. This is probably because their sensing mechanisms are different. It is known that, for n-type semiconductors, surface oxygen species play important roles in the surface sensing reactions. In the case of our PTh/hs-SnO₂, the surface of SnO₂ is covered with PTh, which may potentially cover the active sites and oxygen species. Finally, the response of the hybrids is lower than that of pure SnO₂.

Conclusion

PTh and its derivatives may have a vital role in modifying electrode and as active layer for the chemical sensor materials due to their thermal stability, excellent optical and electrical characteristics while retain good mechanical properties. However, some drawbacks such as poor stability, solubility, and low yield. Remarkably, the hybridised with of another nanomaterial like graphene, carbon nanotubes and metal oxide into the PTh matrix enhances the electrochemical stability of the sensor compared to similar nanomaterials without the nanocomponent and also the conductive polymer itself. Therefore, the combination of conductive fillers such as carbon nanomaterials and inorganic nanoparticles in a polymer matrix is very strategic for sensor efficiency. Combining the features of these three materials into a single material enhances the mechanical properties and sensor performance. The nanocomponent promotes the charge transfer, increases the active sites of the modified electrode surface as a results increase in the sensitivity towards the targeted gas or chemicals.

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