FASCINATING ADVANCEMENTS IN POLYTHIOPHENE AND ITS DERIVATIVES-BASED NANOCOMPOSITES

Abstract

As the realm of nanotechnology continues to push the boundaries of materialscience, the integration of conductive polymers into nanocomposites has emerged as a captivating avenue for innovative research. One class of polymers that has garnered significant attention is polythiophene and its derivatives. The synthesis and utilization of polythiophene-based nanocomposites have opened up exciting possibilities in fields ranging from electronics to energy storage. This review explores the recent advancements in polythiophene and its derivatives-based nanocomposites, highlighting their synthesis, properties, and applications.

Keywords: Conducting polymer, Polythiophene, Nanocomposites

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I. INTRODUCTION

Conducting polymer (CPs) is a category of organic polymer that conducts electricity. They are made up of aromatic rings like naphthalene, phenylene, pyrrole, anthracene and thiophene in which C-C are connected through single bonds [1,2]. Before 1974, polymers considered as insulating materials due to inaccessibility of free electrons. But nearly 50 years back, the scenario has completely changed when H. Shirakawa, first time synthesized polyacetylene with semiconducting properties and later on in 2000, they received the Nobel Prize in Chemistry for their groundbreaking work [3-5]. Thereafter, various CPs have been developed to meet the needs of industrial communities. These organic polymers exhibit electrical conductivity due to presence of conjugated bond with delocalization of π electron. In their undoped condition, these polymers can either be insulating or semiconducting and have a large band gap. But these materials can be changed into conductive mode by oxidation or reduction reactions which result in formation of delocalized charge carriers. Hence, the researchers concentrate their work on these organic polymers as a consequence of mechanical flexibility, low density, low cost and their vast electrical properties [6, 7]. Polythiophene (PT) comes under the above-mentionedcategory and was developed by Alan J.Heeger, having the molecular formula $(C_4H_2S)_{n.}$ It gained significant attention to uplift the industries and research areas due to its mechanical flexibility, better thermal stability, high environmental stability, low cost, low and less energy band gap [8,9]. Polythiophene can be synthesized in the form of powder as well as in film form using polymerization of thiophenes. The main disadvantage of this polymer is lack of solubility which restricts its process ability. Thus, one class of conducting polymers that has garnered significant attention is polythiophene and its derivatives which are water soluble, high electrical conductivity and can be used as electrochemical sensors. From the reported data, it has been concluded that, the bandgap in polythiophene and its derivatives is significantly less than that of other polymers. It was observed that doping can alter their band structures [10]. Therefore, a new class of polythiophene and its derivatives with various nanomaterials are introduced to form electrochemical sensors. The synthesis and utilization of polythiophene based nanocomposites have opened up exciting possibilities in fields ranging from electronics to energy storage. This review explores the recent advancements in polythiophene and its derivatives-based nanocomposites, highlighting their synthesis, properties, and applications [11].

The synthesis of polythiophene and its derivatives-based nanocomposites involves combining polythiophene polymers or their derivatives with various nanomaterials to create hybrid materials with enhanced properties. These nanocomposites can be tailored for specific applications, likeelectronics, energy storage, sensing, and more. Here, we will outline a general approach to the synthesis of polythiophene-based nanocomposites:

1. **Selection of Polythiophene and Nanomaterials:** Choose a suitable polythiophene polymer or its derivative based on the desired properties and application requirements. Common polythiophene derivatives include poly(3-hexylthiophene) (P_3HT), poly(3,4-propylenedioxythiophene)(PProDOT), and poly(3,4-ethylenedioxythiophene) (PEDOT).

   Select appropriate nanomaterials likecarbon nanotubes, metal oxides (MO), nanoparticles, nanotubes, graphene, or polymers that will serve as the matrix or support for the polythiophene component.

The methods employed to create nanocomposites are pivotal in determining the final product's morphology, properties, and potential applications. The preparation of nanocomposites can be done by different methods as mentioned below:

- **Simultaneous Redox Reactions**: This method involves one-step processes where both the polymerization of conducting polymers (CPs) and the formation of nanoparticles occur simultaneously.

- **In-situ Polymerization:** In this approach, pre-synthesized nanoparticles are blended into monomer solution, which is then subjected to chemical or electrochemical polymerization. This technique facilitates the controlled incorporation of nanoparticles into the polymer matrix [12].

- **Chemical Vapor Deposition (CVD)**: In CVD, precursor molecules are thermally decomposed on a substrate to form a thin film.Polythiophene precursors can be vaporized, and the resulting species can be deposited onto the surface of nanomaterials, forming a conformal coating.

- **Template-Assisted Synthesis**: Templates such as porous materials or sacrificial structures can be used to guide the formation of polythiophene-based nanocomposites with controlled structures.

- **Solution Mixing or Dispersion**: Polythiophene polymers or their derivatives can be dissolved in suitable solvent, and the nanomaterialscan be dispersed in same solvent.

- The polymer solution and nanomaterial dispersion are then mixed together and processed to remove the solvent, leaving behind a solid nanocomposite material.

- There are some more methods used for synthesis of Polythiophene and its composites. Chemical reactions commonly yield bulk powdery nanomaterials that can be readily upscaled. In contrast, electro-polymerization confines reactions to electrode surfaces, resulting in composite films deposited on the electrode's surface.

  Obtaining significant quantities of nanomaterials through electrochemical methods is challenging, and the composition and properties of the nanomaterials can undergo slight changes during prolonged electrodeposition. This phenomenon is particularly noticeable during extended electrodeposition periods due to continuous alterations in the surface morphology and electrode resistance, as the film thickness increases.

- As a result of these factors, the electrochemical technique is often selected for the precise synthesis of nanocomposites with controlled morphologies and for the fabrication of micro sized or thin-layer devices. Additionally, electrochemical polymerization offers several well-established advantages, given that the electrochemical parameters can be fine-tuned to regulate both the film thickness and other characteristics of the polymer nanocomposite films.

- Overall, the synthesis of polythiophene and its derivatives-based nanocomposites involves a range of techniques, each with its advantages and challenges. The choice of synthesis method depends on the specific application, desired properties, and the compatibility of the polythiophene and nanomaterial components. Successful synthesis leads to nanocomposites with tailored properties, making them valuable materials for a wide array of technological advancements.

II. THE PROPERTIES OF POLYTHIOPHENE AND ITS DERIVATIVES CAN ALSO BE MODIFIED BY FOLLOWING METHODS

1. **Surface Modification and Functionalization**: Surface functionalization of the nanomaterials can enhance compatibility with polythiophene and improve the dispersion within the matrix. Functional groups such as carboxylic acids, amines, or silanes can be introduced onto the nanomaterial surface to create reactive sites for covalent attachment to polythiophene or its derivatives [13].

2. **Layer-by-Layer (LbL) Assembly**: LbL assembly involves the sequential deposition of alternating layers of polythiophene or its derivatives and oppositely charged polyelectrolytes or nanomaterials.This method allows specific control over the composition and thickness of nanocomposite layers, enabling the fine-tuning of properties.

3. **Electrospinning**: Electrospinning involves the use of an electric field to create nanofibers from a polymer solution. Polythiophene solutions can be electrospun to form nanofibers, and nanomaterials can be incorporated either by blending them with the polymer solution or by post-deposition on the nanofibers.

One of the most remarkable features of polythiophene-based nanocomposites is their exceptional electrical conductivity. Polythiophene's highly conjugated structure enables effective charge transport, making these nanocomposites suitable for applications in optoelectronics and organic electronics. Thin-film transistors, organic solar cells, and light-emitting diodes (LEDs) have been benefitted from the remarkable conductive properties of these materials. In 2010Zhu et al. [14] undertook the synthesis of aPTh/TiO_2 nanocomposite considered for the photocatalytic degradation of dye (methyl orange) on exposure of ultraviolet (UV) light. Their methodology incorporated a customized UV-irradiation apparatus equipped with 10W germicidal lamps emitting at maximum wavelength of 253.7 nm, facilitating catalytic process. The transformation in Methyl Orange concentration was quantified through absorbance measurements utilizing a UV-visible spectrophotometer.TiO_2 solely absorb between 0-400 nm regions, while nanocomposite PTh/TiO_2 displayed absorption across the 200-800 nm wavelength range. This characteristic suggested the nanocomposite's capacity for solar light activation. Notably, beyond the photodegradation process, these nanocomposites exhibited surface adsorption capabilities for the dye, an attribute influenced by the weight ratio of PTh to TiO_2. Interestingly, the adsorption capacity initially escalated with an increasing PTh ratio, and to decline subsequently. This phenomenon correlated with the intricate structural attributes of the nanocomposite system. During UV light testing, the sole use of PTh as a catalyst yielded insignificant MO degradation (< 5.0%). In contrast, pure TiO_2

demonstrated 48.5% MO degradation, while the PTh/TiO_2 nanocomposite exhibited a more substantial 56.6% degradation. The degradation rate initiated at a swift pace and subsequently stabilized due to dye adsorption on the catalyst's active sites. However, PTh/TiO_2 nanocomposites boasting more PTh content exhibited restricted catalytic activity. This outcome arose because PTh, once adhered to the TiO_2 surface, occupied a significant portion of the active sites, hindering the MO molecule's access to the TiO_2 active sites for degradation. The surface characteristics emerged as pivotal in influencing photocatalytic traits; intricately linked to the PTh to TiO_2 weight ratio. In 2011, Jung et al. [15] conducted a study in which they synthesized nanocomposites consisting of Ag and PEDOT. The resulting Ag/PEDOT nanocomposites exhibited a core-shell structure, with Ag nanoparticles well evenly distributed throughout the PEDOT polymer matrix, contributing to a high surface area and excellent electrical conductivity. The researcher's usedcyclic voltammetry (CV) to calculate its electrochemical properties. The sample so formed had the highest charge capacity at 209 mAh/g even after the 20th cycle, with a value of 291 mAh/g on the first cycle.These nanocomposites' distinctive shape aided in the transport of lithium ions, thereby enhancing the overall electrochemical performance. This enhancement resulted from facilitated mass transfer and effective charge transfer at the interface. Additionally, cyclic voltammetry was conducted with a scan rate of 0.05 mV/s, covering the voltage range from 0 to 2.8 V. To increase the surface area, Ag/PEDOT core-shell nanocomposites were synthesized using a one-pot reduction approach for potential anode material applications. The incorporation of PEDOT as a buffering agent played a vital role in preventing the agglomeration of Ag particles, thereby enhancing the dispersion and stability of the Ag particles.

In a study by Chandra et al.[16], it was observed that the PTh/TiO_2-Cu composite, produced using a sol-gel method, exhibited a robust interaction at the interface between PTh and TiO_2-Cu components. The absorption spectrum of the TiO_2-Cu composite displayed a range between 450 nm and 500 nm. Similarly, the absorption spectrum of the PTh/TiO_2-Cu composite showed an extended range, indicating a strong interaction between composites. This interaction is anticipated to facilitate efficient transfer of charge from PTh to TiO_2-Cu, consequently enhancing the photocatalyticity. When assessing the degradation, it was observed that the rate of rhodamine blue (RhB) degradation increased with higher PTh content in the composite, reaching its peak at a polymer loading of 1.0 wt. %. Subsequently, degradation rate diminished as polymer loading further increased to 2.0 wt. %, suggesting the presence of an optimal threshold for PTh content to achieve its most favorable catalytic properties. Moreover, the content of PTh within TiO_2-Cu demonstrated a substantial impact on increasing the photocatalyticity. Energy storage applications have also seen the integration of polythiophene-based nanocomposites. By incorporating these materials into supercapacitors and lithium-ion batteries, researchers have achieved enhanced energy storage capacities and prolonged cycle life. The synergistic effects produced from mixing of polythiophene with nanomaterials like graphene, carbon nanotubes, and MOhas led to remarkable improvements in energy storage performance. Moreover, polythiophene-based nanocomposites exhibit excellent mechanical flexibility, making them ideal candidates for flexible and wearable electronics. Their compatibility with various substrates, combined with their ability to maintain electrical performance under strain, positions them as key players in the development of next-generation electronic devices.

In 2019, P. Pascariu et al. synthesized a thin film of PTh/Ni nanocomposites using electrochemical oxidative polymerization method. The conductivity can be tuned by changing the composition of Ni nanoparticles in the composites. The electrochemical performance was studied by changing the Ni content. These nanocomposites with the highest composition of nickel were found to be more electrochemical active, maximum specific capacitance with value 3000 F g^{-1} and the fastest discharging process (200 s).These composites demonstrated high electrical conductivity while maintaining its electrochemical stability [17]. In 2020, Wang et al. prepared nanocomposites of Polythiophene/Fe_3O_4 with different morphologies using oxidative polymerization method. Here, PTh restrict the agglomeration of Fe_3O_4. They have reported that the Fe_3O_4 incorporated in PTh improved electrical conductivity (1.4×10^{-5} S/cm) of titled nanocomposite. The authors concluded that the specific capacitance of nanocomposite with spherical morphology (SA) is two times more than the nanoparticle containing flower like (FA) Fe_3O_4. This is due to distribution of SA Fe_3O_4 is more uniformly distributed on the surface of PTh [18].Melo et al. reported the GR/PTh nanocomposites with different mass composition for their fruitful application as super capacitors. Cyclic voltammetry (CV) technique was used to extract capacitance curve of different nanocomposites. Furthermore, a detailed study on impedance spectroscopy was also carried out. From this data, it was confirmed that composite in the ratio of 1:1 showed a high value of specific capacitance as compared to pure Graphene which make it potential candidate for making electrode in supercapacitors. Inspite of sole polymer, the composite of graphene and polythiophene exhibited enhanced cyclic stability [19].In 2018; H. Vijeth published an article in which they have prepared Polythiophene/Al_2O_3 nanocomposites using chemical polymerization method. The formation of sample was confirmed by AFM study. From the observation, it was concluded that the titled nanocomposite can be utilized in application of supercapacitor. Using voltammetry technique, its specific capacitance was calculated having a value of 757 F/g and 654.5 F/g for PTHA and PTh nanocomposites at 30 mV s^{-1} respectively. CV studies revealed that the prepared composites are suitable for making electrodes in supercapacitor [20]. Beyond electronics and energy storage applications, polythiophene-based nanocomposites have demonstrated promise in sensing and catalysis. The high surface area of nanocomposites provides abundant sites for analyte adsorption in sensing applications, while the conductivity of polythiophene enhances the efficiency of catalytic reactions [21, 22]. PTh and its derivatives, have a much narrower bandgap compared to other polymers, and various dopants can be used to change their band gap [23]. Hence, PTH with its compounds can be mixed with various nanomaterials to meet the requirements of electrochemical sensors that demand a low detection limit, fast response, strong sensitivity, appropriate selectivity, repeatability, good stability, and ease of production. In terms of CPs, we are primarily interested in PTh and its composites, like P3MT, P3T, PEDOT, ProDOT, etc. The important monomers, including chalcogenides (MoS_2), metals, MO, and carbon nanomaterials (GrGO, and MWCNTs), are also discussed in this article.

III. PTH-BASED BINARY/ TERNARY NANOCOMPOSITES

There have already been many electrochemical sensors developed employing PTh binary and ternary nanocomposites. A few recent studies conducted by diverse researchers in this area are listed in Table 1. Faisal et al. [24] synthesized a glassy carbon electrode (GCE) with Polythiophene/ZnO nanocomposites by the sol-gel technique, which was then polymerized chemically through oxidation for sensing hydrazine (N_2H_4). Using, CV technique they revealed that synthesized nanocomposites were more sensitive towards hydrazine detection than pure GCE/ZnO.

They demonstrated that when concentrations of hydrazine lies in range 0.5 to 48 M, prepared nanocomposites show excellent sensitivity and correlation coefficient ($R^2 = 0.9983$).The electrochemical analysis at S:N = 3:1 revealed that the LOD was 0.207 μM, which is much less than that found in several earlier investigations. Further, they revealed that synthesized electrodes were found to have excellent repeatability and operational stability. Singh et al. [26] discussed Fe_3O_4/PTh nanocomposites (Superparamagnetic substances) for amperometric detection of H_2O_2.They reported the synthesis of nanocomposites of Fe_3O_4/PTh, by insitu synthesis method by chemically polymerizing thiophene in the atmosphere of Fe_3O_4 nanoparticles. Because of the combined effect of the conductive capabilities of PTh and the magnetic properties of Fe_3O_4, the modified electrode has a high sensitivity to H_2O_2 with a LOD of 5 μM.. Harraz et al. [27] developed a PTh/α-Fe_2O_3 composite film-based liquid methanol electrochemical sensor.

The CP was created by oxidatively polymerizing thiophene monomer with anhydrous $FeCl_3$. A p-type semiconductor was used as a dopant to create the film. PTh, an organic substance, and $FeCl_3$, an n-type semiconductor, enhanced the target analyte's adsorption and diffusion onto the altered electrode surface. An electron was created as a result of this action. Over the concentration ranging from 5−1000 mM, the LOD was 1.59 mM. Saljooqi et al. [28] reported a DNA biosensor (label-free) for the detection of mitoxantrone using PTH and Ag nanoparticles supported on multiwall carbon nanotubes. Several techniques, including SEM, EDX, and XRD, were used to characterize the morphology of the nanocomposites for modifying GCE. The constructed sensor displayed a broad dynamic concentration range from 0.05 to 100.0 M utilizing differential pulse voltammetry, with detection limits (3 Sb/m) of 13 nM for mitoxantrone, an anticancer drug. Inagaki et al. [29] used self-assembly to create a PTH/Au/CNT electrode for detecting the presence of dopamine (DA). PTH, CNTs, and AuNPs create nanocomposites t the liquid-liquid interface. Different reaction periods were examined, and the materials were characterized using a variety of techniques to understand their structural and electrochemical characteristics. Electrochemical characteristics were examined via CV (cyclic voltammetry). When compared to PTH/Au, synthesized nanocomposite had the highest sensitivity of 19.492 μA L μmol^{-1} and LOD of 0.69 μA L μmol^{-1}. This was because the addition of CNT to film increases reaction time as compared to film without CNT.

Table 1: Electrochemical Sensors Employing Pth Binary and Ternary Nanocomposites

Nano component	Analytes of interest	Mode of Synthesis	Mode of Detection	Reference
PTh/ZnO	N_2H_4	sol-gel method followed by in situ chemical polymerization	Amperometric	[24]
CSA-PTHA	N_2H_4	chemical oxidative	Amperometric	[25]

		polymerization		
Fe_3O_4/PTh	H_2O_2	”	Amperometric	[26]
PTH/α-Fe_2O_3	Liquid CH_3OH	Oxidative polymerization following Sol-gel method	current-potential	[27]
MWCNT-Ag-PTh	mitoxantrone	Solution Mixing or Dispersion	differential pulse voltammetry	[28]
PTh/AuNPs/ CNT	Dopamine	liquid-liquid interfacial reaction	differential pulse voltammetry	[29]

IV. PTH DERIVATIVE-BASED BINARY NANOCOMPOSITE SENSORS

PTH compounds like poly terthiophene (P3T), ProDOT, and PEDOT nanocomposites are commonly employed in prospective sensor applications. Table 2 depicts the use of these PTh derivatives as electrochemical sensors. Maouche et al. [30] created a P3T-MNP/Pt electrode for sensing AA (ascorbic acid), which was formed by modifying the Pt electrode with P3T and further doping with MNP (nanoparticles of metal such as Co, Au, Ag, etc.). They reported that these electrodes were found to exhibit better catalytic activity for sensing AA in comparison with PTh-modified thin films. The reported electrode was found to have greater oxidation current for the detection of ascorbic acid than other metallic P3T-MNP/Pt electrodes. The peak observed at 367.60 eV in XPS was attributed to the 3D orbital of Ag, indicating that Ag nanoparticles were effectively trapped in the CP matrix.Poly(3-methylthiophene) (P3MT) is another form of Polythiophene derivative. It is commonly utilized in the fabrication of sensors. The introduction of chain of alkyl atom having an electron donor inductive effect greatly reduces the oxidation potential of corresponding polymers [31]. M. Arvand et al. [32] created an Ag-NPs/P3MT modified electrode by electro-polymerizing P3MT in the presence of $AgNO_3$ on the surface of GCE for sensing galantamine hydrobromide (Gal). The fabricated electrode displayed exceptional electrochemical catalytic activity and considerably increased the oxidation peak current of Gal in comparison to pure and modified P3MT electrodes. When used with differential pulse voltammetry to detect Gal, the suggested electrode demonstrated good sensing capability over a concentration range of 1.0–700 µM with an LOD of 0.18 µM. Last but not least, the superb results demonstrated that the modified electrode can be successfully employed to measure quantity of Gal in human fluid near the spinal cord and brain. On this premise, F. Tian et al. [33] developed a range of PEDOT-Gr composites using electrochemical polymerization of PEDOT on Gr (graphene) sheets. The formation of composites of PEDOT-Gr was validated by XRD and FTIR spectroscopy. SEM results confirmed the production of 1D PEDOT structures that were about 200 nm in diameter. For concurrent detection of nitrite, resorcinol (RC), hydroquinone (HQ), and catechol (CC), 1D PEDOT-Gr composites were employed. These composites demonstrated that the separation between peaks of HQ, CC, RC and nitrite and RC was 108 mV, 392 mV, and 188 mV, respectively. The strong electrocatalytic activity, quick response time, high selectivity, and extended life of the 1D PEDOT-graphene composite were all demonstrated. Hybrid composite PMe Th consisting of conducting polymers poly(3-methythiophene) and PCN-222 (Fe) was fabricated by Y. Chen et al. [34] for L-dopa (levodopa) detection by using in situ polymerization. Poly (3-methythiophene) was used to collect and transfer the charge, and PCN-222(Fe) served as the electrocatalytic site. The composite so formed had a great sensitivity of 1.868 and 0.778 μA· μM^{-1} cm^{-2} for concentrations ranging, correspondingly from 0.05 to 7.0 and 7.00 to 100 μmol· L^{-1} for L-dopa detection.

The LOD found for these sensors was 2 nmol/L. These were found to exhibit great stability after 120 cycles.By combining the special qualities of ZrO_2 and PEDOT NPs, Arvand et al. [35] created an electrochemical method for detecting progesterone. The nanocomposite was created by using the CV approach of electrodeposition. The surface areas of the modified electrode and the unmodified electrode were 0.035 cm^2 and 0.017 cm^2, respectively. The reason behind the greater surface area of the modified electrode was explained in terms of the strong compatibility of PEDOTs with ZrO_2 NPs. Distinct oxidation peak at 1.05 V was observedin concentration range lying between 1 to 100 nM and 100 to 6 $\times 10^3$nM using DPV. It was determined that the LOD was 0.32 nM. Without complicated sample preparation, it was successfully used to determine the presence of progesterone in pharmaceutical and biological specimens.

Table 2: Electrochemical Sensors Employing Pth Derivates

Nano components	Method of detection	Analytes of interest	Linear range	References
P3T/MNPs	Square wave voltammetry	Electropolymerization trailed by immersing the film produced in solution having metallic particles.	……	[30]
AgNPs/P3 MT	Differential pulse voltammetry	Insitu electropolymerization	1.0−700 μM	[32]
PCN-222(Fe) P3 MT	Differential pulse voltammetry	in situ chemical polymerization	0.05−7.0 μmol L^{-1}& 7.00−100 μmol L^{-1}	[33]
PEDOT/ZrO_2	Differential pulse voltammetry	One-pot electrochemical synthesis	1−100 & 100−6 × 10^3nM	[34]
PEDOT-Gs	Differential pulse voltammetry	In situ electropolymerization	5–250, 6–2000, 0.4–350, and 2–2500	[35]

			μM for HQ, RC CC, and NO_2^- respectively	

V. CONCLUSION

Nanocomposites composed of PTh exhibit enhanced optical, electrical, thermal, mechanical, and other properties in comparison to pure PTh. However, sometime, the added component also has a tendency to reduce the material's electrical conductivity. This comprehensive article encapsulates a variety of methodologies employed in crafting PTh nanocomposites and producing devices for potential applications. These applications span chemical sensing, display technologies, rechargeable batteries, optical sensing, light-emitting diodes (LEDs), photovoltaics/solar cells, supercapacitors, transistors, electromagnetic interference (EMI) shielding, and more.

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