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Preparation and Applications of Polythiophene Nanocomposites

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Abstract: Polythiophene (PTh) nanocomposites are unique and attractive materials because of their excellent electrical, electro-chromic and electronic properties with high environmental and thermal stabilities. Polythiophenes and their nanocomposites are gaining importance and use as conducting materials in the industries and in a wide range of potential applications including chemical/optical sensors, light-emitting diodes, display devices, photovoltaics/solar cells, transistors, rechargeable batteries, supercapacitors, EMI shielding etc. A comprehensive review on the preparation of nanocomposites based on polythiophenes using several types of materials such as metal oxides nanoparticles, metal nanoparticles, graphene, carbon nanotubes etc. and their potential applications in various scientific fields have been discussed in this article.

Keywords: Polythiophenes, Nanocomposites, Sensors, *In-situ* polymerization, Photo-catalyst.

الخلاصة: المركبات النانوية من البوليثيوفين (PTh) هي مواد فريدة وجذابة بسبب خصائصها الكهربائية والكهروكرومية والإلكترونية الممتازة ذات الاستقرار البيئي والحراري العالي. تكتسب البوليثيوفين ومركباتها النانوية أهمية واستخدامها كمواد موصلة في الصناعات وفي مجموعة واسعة من التطبيقات المحتملة بما في ذلك أجهزة الاستشعار الكيميائية / البصرية، الثنائيات الباعثة للضوء، أجهزة العرض، الخلايا الكهروضوئية / الخلايا الشمسية، الترانزستورات، البطاريات القابلة لإعادة الشحن، المكثفات الفائقة، EMI التدريع وما إلى ذلك. تمت مراجعة شاملة حول تحضير المركبات النانوية على أساس البوليثيوفين باستخدام عدة أنواع من المواد مثل الجسيمات النانوية أكاسيد المعادن، والجسيمات النانوية المعدنية، والجرافين والأنابيب النانوية الكربونية وما إلى ذلك. ومناقشة تطبيقاتها المحتملة في مختلف المجالات العلمية.

1. Introduction

Conducting polymers (CPs) and their nanocomposites (NCs) are particularly interesting materials for a number of applications like structural, electronic, thermal, electrochemical, electromagnetic interference shielding (EMI) etc. either in the partially oxidized or in the reduced state. Conducting polymers have extended π-systems and are highly susceptible to chemical or electrochemical oxidation or reduction. Thus the electrical and optical properties of such polymers could precisely be altered by controlling carefully the process of oxidation and/or reduction. Since these reactions are often reversible, it is possible to systematically control the electrical and optical properties with a great deal of precision switching from a highly insulating state through semiconducting to the highly conducting state with greater thermal stability. Thus conducting polymers can be perceived as macromolecules having the fully conjugated sequence of bonds along the backbone which acquires a positive or negative charge by oxidation or reduction process [1-6].

With the advent of many more discoveries in the field of conducting polymers, today we have a variety of polymers which have shown to exhibit electrical conductivity. Currently, conducting polymers (CPs) such as polypyrrole (PPy), polyaniline (PAni), polythiophene (PTh) and their derivatives are promising materials for the preparation of nanocomposites (NCs) materials and the devices based on them. Nanocomposites are a special class of materials originating from suitable combinations of two or more such nanoparticles or nanosized objects resulting in materials having unique properties and the wide application potential in diverse areas. Novel properties of nanocomposites can be derived from the successful combination of the characteristics of parent constituents into a single material [7-18].

Many investigations regarding the development of the incorporation techniques of the nanoparticles into the polymeric matrices have been published [19]. In most of the cases, such combinations require blending or mixing of the components, taking the polymer in solution or melt form [20]. Resulting nanocomposites have found successful applications in versatile fields *viz.* battery cathodes [21], microelectronics [22], nonlinear optics [23], sensors [24] etc. Among conducting polymers composites, the polythiophene nanocomposites have received much more attention from scientific communities and researchers in recent years because of their unique electrical, electro-chromic and electronic properties with high environmental and thermal stabilities [25–27]. Polythiophenes and their nanocomposites are the important and most frequently used CPs in the industries with a wide range of potential applications including chemical & optical sensors, light-emitting diodes (LEDs), display devices, photovoltaic solar cells and transistors [28-29].

As a result, a large number of papers on PTh nanocomposites have been published in recent times. The present review summarizes the systematic progress in the preparation and applications of polythiophene nanocomposites in the field of sensor, photocatalyst, rechargeable batteries, supercapacitors and EMI shielding etc. For the convenience of readers, the present discussion is divided into several categories depending upon the composite materials and the application aspects. We hope this article will provide the readers a better understanding of the recent developments and advancements of polythiophene nanocomposites research.

2. Preparation of Polythiophene Nanocomposites

The synthetic strategies for the preparation of nanocomposites play a very important role as they impinge upon the resulting product in terms of morphology and properties and consequently their applications. Most of the methods that are in use for nanocomposites preparation are generally based on two routes: (i) one-step redox reactions where simultaneous polymerization of CPs and formation of nanoparticle takes place or (ii) *in-situ* polymerization where pre-synthesized nanoparticles are mixed into the monomer solution followed by chemical or electrochemical polymerization.

Chemical reactions usually produce powdery nanomaterials in bulk and can easily be scaled up. On the other hand, electro-polymerization restricts the reactions on the surfaces of electrodes; results in films of the composites deposited on the electrode surface. Thus it is difficult to get a large amount of nanomaterial by electrochemical techniques and the composition and property of the nanomaterials changed slightly during the electrochemical growth process, especially in the case of long-time electrodeposition. This is mainly due to the surface morphology and resistance of the working electrode continuously changing with increase in film thickness. Therefore, the electrochemical technique is usually chosen for the purposes of synthesizing nanocomposites with controlled morphologies and fabricating microsized or thin-layer devices. In addition, electrochemical polymerisation has a number of well-known advantages because the electrochemical variables can be adjusted to control the film thickness and other characteristics of the polymer nanocomposite films.

2.1 Nanocomposites of polythiophene with metal oxide nanoparticles

In-situ chemical polymerization is the most commonly employed method because it provides a better size and shape control than the one-step redox method. Biswas *et al.* [30] successfully prepared polythiophene (PTh) and PTh/Al_2O_3 nanocomposite in bulk and in solution (chloroform) via chemical oxidative polymerization using $FeCl_3$ as oxidant and they observed higher yield in the later case. They observed that the high yield of PTh (70–80%) could be achieved when thiophene was added to $FeCl_3$ solution directly at temperatures above 60°C. The results showed that the conductivities of PTh and PTh/Al_2O_3 nanocomposite were of the order of 10^{-3} Scm^{-1} for both the I_2 doped samples.

Martin *et al.* [31] synthesized PTh/TiO_2 nanocomposite via *in-situ* chemical polymerization having core-shell morphology. They investigated the electrochemical and photoelectrochemical properties of the nanocomposite.

Xu *et al.* [32] synthesized SnO_2 hollow spheres (hs)/polythiophene hybrid materials by an *in-situ* chemical oxidative polymerization method. TEM micrographs of hs-SnO_2 and hs-

SnO_2/(20%)PTh hybrids showed that the hs-SnO_2 was successfully synthesized with an average size of about several hundred nanometres and had a rough morphology. It was observed that hs-SnO_2 particles got encapsulated partly by PTh.
Huang *et al.* [33] also synthesized PTh/WO_3 nanocomposites by *in-situ* chemical polymerization method. By TEM micrographs of pure WO_3 and PTh/WO_3 hybrid, it was observed that the WO_3 has an average particle size of about 20−30 nm and WO_3 particles were well encapsulated by PTh with a thickness of about several nanometres. Thermal stability of the hybrids was examined by TG analysis. In the case of pure PTh, the mass decrease started at approximately 290°C and almost decomposed completely when the temperature was up to 650°C. Different from pure PTh, the 10 wt% PTh/WO_3 hybrid was initially stable up to 320°C which was 30°C higher than the pure PTh. The delay of the decomposition process of the hybrid indicates that the thermal stability of the PTh/WO_3 hybrid is better than that of the pure PTh.

Barkade *et al.* [34] prepared PTh/SnO_2 nanocomposite via ultrasound-assisted *in-situ* chemical oxidative polymerization by using anhydrous $FeCl_3$ as the oxidant and dopant in batch mode. By TEM image, it was observed that all SnO_2 nanoparticles got encapsulated by PTh and no uncovered SnO_2 nanoparticles were observed. The SnO_2 nanoparticles were uniformly dispersed in PTh. This can potentially be attributed to the ultrasonic irradiation used during polymerization which may break the aggregation of SnO_2 nanoparticles.

Tahmasebi *et al.* [35] has successfully modified the surface of Fe_3O_4 NPs by polythiophene using self-assembly of polythiophene onto Fe_3O_4 NPs via oxidative polymerization of thiophene monomers in the presence of Fe_3O_4 NPs and using $KMnO_4$ as oxidant. They reported their application as a new sorbent in magnetic solid-phase extraction (MSPE) for extraction and preconcentration of plasticizer from real water samples. They observed that the coating of NPs with polythiophene can increase the adsorption ability of the target analytes, improve stability of the NPs and their dispersibility in aqueous media.

Khatamian *et al.* [36] synthesized the nanocomposites of polythiophene (PTh)/zinc oxide (ZnO) nanoparticles with different PTh wt%, (2%, 4%, 6%, 10% and 20%) by an *in-situ* chemical oxidative polymerization method. They evaluated photocatalytic activities of the nanocomposites by the degradation of methyl orange (MO) aqueous solution under visible light and sunlight irradiation. They observed that at a higher percentage of PTh, the photodegradation activity was improved because of high adsorption capacity.

2.2 Nanocomposites of polythiophene with graphene and carbon nanotubes (CNTs)

Graphenes are atom-thick layers of carbon exhibiting exceptional properties. These layers or sheets when rolled at specific chiral angles form carbon nanotubes (CNTs). CNTs possess extremely high aspect ratio and show extraordinary thermal, electrical and mechanical properties which are dependent on the rolling angle and radius. When incorporated into PTh, they improve the properties and also render them useful in various applications.

Karim *et al.* [37] successfully synthesized polythiophene (PTh)/single-wall carbon nanotubes (SWNTs) nanocomposites by the *in-situ* chemical oxidative polymerization method. The structure and properties of the nanocomposite (PTh/SWNT) were characterized with elemental analysis, x-ray photoelectron spectroscopy, Raman spectroscopy, Fourier transform infrared, ultraviolet-visible spectroscopy, field emission scanning electron microscopy, thermogravimetric analysis, x-ray diffraction and transmission electron microscopy. TEM photograph showed the tubular morphology of the PTh/SWNT nanocomposite. SWNTs were used as self-assembly hard templates for the formation of one-dimensional, co-axial PTh/SWNT nanocomposite. The polymer was found to be tightly coated only on the surface of the SWNTs. By comparing TEM photographs of the pure SWNTs with the PTh/SWNT nanocomposite, it was concluded that nanocomposite was very thick (60–80 nm in diameter) and the surface was not smooth. Field emission scanning electron microscopy and transmission electron microscopy analysis revealed that the PTh/SWNT nanocomposite as core (SWNTs) and shell (PTh) hybrid structures. They reported that the electrical conductivity of resulting PTh/SWNT nanocomposite is ~0.41 Scm^{-1} at room temperature which is greater than the conductivity of pure PTh ~1.67×10^{-6} Scm^{-1} synthesized under identical conditions.

In another study, Yusuf *et al.* [38] prepared polythiophene and single-walled carbon nanotube (PTh/ SWCNT) nanocomposite by chemical oxidative polymerization using anhydrous ferric chloride as oxidant and chloroform as solvent. Comparison of PTh and PTh/SWCNT nanocomposites by SEM, the presence of a random network of interconnected bundles packed underneath the outermost polymer pellet in the PTh/SWCNT nanocomposite. The observed conductivity of PTh/SWCNT nanocomposite was found four times greater than that of polythiophene and the real part of the permittivity (ε) of PTh/SWCNT nanocomposite was much higher than that of pure polythiophene. Further, it was observed that the electrical behaviours of PTh could be modified by employing single-walled carbon nanotubes and also a semiconducting peculiarity of these nanotubes bring a semiconductor-like polymer nanocomposite.

Lee *et al.* [39] synthesized nanocomposites of conducting polythiophene with the host filler multi-walled carbon nanotubes (MWNTs) by the *in-situ* γ radiation-induced chemical polymerization method at room temperature. The resultant morphology of the nanocomposite (PTh/MWNT) structures was characterized by field emission scanning electron microscopy with the energy dispersive spectroscopy, Fourier transform infrared, thermal gravimetric analysis, x-ray photoelectron spectroscopy and transmission electron microscopy. The morphology observed by transmission electron microscopy of the MWNT and PTh/MWNT nanocomposite was tubular. Also, interfacial entrapment between the PTh and MWNT showed the polythiophene is coated on the surface of the carbon nanotube. It was found that the tubular inner part was mainly the compound of MWNT and the outer coated surface was conducting polythiophene with the variable thicknesses (20–50 nm diameter) and their surfaces are not smooth. PTh/MWNT nanocomposite showed improved thermogravimetric stability as compared to PTh upto 800°C. The conductivity of the samples was measured by standard four-point probe methods. The conductivity of the PTh/MWNT nanocomposite was found to be 3.71 Scm^{-1} which is much larger than the usual value of the PTh ($\sim 1.23\times10^{-4}$ Scm^{-1}).

Wang *et al.* [40] have successfully prepared different polythiophene/multiwall carbon nanotube (MWNTs) nanocomposite with 30 wt% and 50 wt% MWNTs by solution mixing (PML), mechanical ball milling (PMM) and *in-situ* composite (PMI). They investigated the morphology, internal structure and thermal stability of the nanocomposites by SEM, XRD, FTIR and TGA. The electric conductivity and Seebeck coefficient of the bulk nanocomposites were simultaneously measured using a Seebeck coefficient/electric conductivity measuring system from room temperature to 393K in the helium atmosphere. Thermal conductivity was also measured by thermal conductivity tester KY-DRX-RW. The nanocomposites prepared by solution mixing (PML) exhibited highest Seebeck coefficient and highest electrical conductivity among those of the composites prepared by these three methods: solution mixing (PML), ball milling (PMM) and *in-situ* composite (PMI). The MWNTs in the composites prepared by PML were better dispersed in the polymer matrix than those in the composites prepared by PMM which leads to higher conductivity. More interfaces between PTh and MWNTs in the nanocomposite prepared by PML due to the better dispersing of MWNTs which leads to higher Seebeck coefficient. However, the nanocomposites prepared by PML showed higher Seebeck coefficient and higher electrical conductivity due to the core-shell PTh-MWNT microstructure formed during the *in-situ* oxidative polymerization of PTh. The MWNTs were coated with PTh and could directly not touch each other leading to its lower conductivity. The results showed that the MWNTs were uniformly dispersed in the polymer matrix and the nanocomposite materials exhibited good thermal stability under 200°C. The TGA results indicated that the thermoelectric properties of the composites could be investigated under 200°C without destroying the structures of PTh. The electrical conductivity for the nanocomposites improves greatly from 2.34 Sm^{-1} to 29.82 Sm^{-1} with increasing the MWNTs content from 10 wt.% to 90 wt.%. The highest conductivity of 29.82 Sm^{-1} is 11 times higher than that of pure PTh. With increasing MWNTs content, the Seebeck coefficient slightly fluctuates, the thermal conductivity slightly increases but the electrical conductivity increases remarkably. From the results, this work suggests that the polymers with high Seebeck coefficient will play an important role in improving thermoelectric performance of polymer/inorganic nanocomposites.

Bora *et al.* [41] reported a new method for the synthesis of polythiophene (PTh)/graphene oxide (GO) nanocomposites by liquid/liquid interfacial polymerization. Polymerization occurred at the interface of two immiscible solvents i.e. *n*-hexane containing thiophene and nitromethane containing GO and an initiator. They observed that PTh/GO nanocomposites exhibited improved thermal stability compared to pure PTh. Both the optical and electrochemical band gap of the nanocomposites found to decrease dramatically on the incorporation of GO into the polymer matrix. Electrical conductivity and the specific capacitance value of the composites was found to be 2.7×10^{-4} Scm^{-1} and 99 Fg^{-1} respectively. By the result obtained they concluded that the PTh/GO nanocomposites prepared using the interfacial polymerization method possessed great promise for a range of potential applications in batteries and optoelectronic devices.

Swathy *et al.* [42] have synthesized the polythiophene-multi walled carbon nanotubes nanocomposites (PTh-CNTs) by *in-situ* chemical oxidative polymerization of thiophene in presence of multiwalled carbon nanotubes using ferric chloride as an oxidizing agent and sodium bis-2-ethylhexylsulfosuccinate (AOT) as an anionic surfactant in chloroform solvent.

2.3 Nanocomposites of polythiophene with multi-component systems

Xie *et al.* [43] have successfully synthesized La-doped barium-ferrite/polythiophene (LB/PTh) nanocomposites by *in-situ* chemical oxidative polymerization. Morphology was investigated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Electromagnetic properties of nanocomposites were tested by four-probe conductivity tester and vibrating sample magnetometer (VSM). The results of XRD indicated that La^{3+} had entered into the lattice of barium ferrite. TEM and SEM studies showed that the nanocomposites have a core-shell structure. SEM images revealed that PTh is deposited on the surface of LB particles which have a nucleating effect on the polymerization of PTh. TEM images also indicated that the ferrite particles are embedded in PTh matrix forming the core-shell structure. The black core is magnetic ferrite particle and the light-coloured shell is PTh in the nanocomposite due to the different electron penetrability. It indicates that the nanocomposite is composed of polycrystalline LB ferrite particles and PTh which is in accordance with the results obtained by FT-IR analysis. It was observed that the electrical conductivity of the nanocomposite decreases with increasing the ferrite particles content. There may be two main reasons for the decrease in electrical conductivity. The first reason may be the insulating behaviour of ferrite particles in the core of nanocomposite hinders the charge transfer in PTh. While the other may be the generation of the stable σ-π bond between PTh and ferrite particles decreases the conjugated π-electron density in PTh. It was also revealed that the nanocomposites showed the hysteretic loops of the ferromagnetic behaviour under the applied magnetic field.

Ge Ma *et al.* [44] successfully synthesized Cu-doped zinc oxide and its polythiophene nanocomposites by the Sol-Gel and *in-situ* polymerization methods respectively. The antibacterial results reveal that the CZ/PTh nanocomposites possess better antibacterial activity compared with CZ because of the photosensitization of PTh to CZ. The antibacterial activity of composites improves with the contents of CZ increasing and there exists certain synergistic antibacterial effect between PTh and CZ instead of mixing CZ and PTh simply.

The metal-ion and nanoparticles can improve the antibacterial efficiency together in which photocatalytic mechanism is the most persuasive among them. The result showed that the conductivity of CZ is much higher than those of ZnO and CuO and the conductivities of CZ/PTh nanocomposites are also higher than those of CZ and PTh. It is because the band gap of CuO (1.70 eV) is much narrower than that of ZnO (3.37 eV).

Wang *et al.* [45] prepared polythiophene/Pd/TiO_2 (PTh/Pd/TiO_2) ternary composite microspheres and applied such a composite to photoelectrochemical (PEC) sensing. TiO_2 spherical aggregates of 200 nm diameter consisting of nanoscale building blocks of TiO_2, have been prepared by hydrolysis of tetrabutyltitanate in a water-in-oil emulsion system ($V_{water}/V_{acetone}$=1/100). Pd species and PTh layer were decorated onto TiO_2 microspherical substrates by reduction of Pd salts and polymerization of thiophene respectively. The high surface area, effective charge transfer and enhanced light absorption of the ternary composite could improve PEC performance under simulated sunlight. The sensitivity, selectivity and stability of the PEC sensor for detecting L-cysteine were much higher than those of the traditional electrochemical sensor. The detection limit of L-cysteine was 9.24 μM in the linear range of 0.31−5.30 mM. Moreover, the results also indicated a good anti-interference and acceptable accuracy in practical application providing a rapid and sensitive detection method.

Mehdinia *et al.* [46] successfully synthesized a magnetic nanocomposite of G/Fe_3O_4/PTh by *in-situ* chemical polymerization. The prepared nanocomposites were used as a novel sorbent for the magnetic solid-phase extraction of polycyclic aromatic hydrocarbons from environmental water samples.

Chandra *et al.* [47] prepared PTh/TiO_2-Cu composite by a sol-gel process. In another study, Chandra *et al.* [48] synthesized polythiophene supported tin-doped titanium nanocomposites (PTh/Sn-TiO_2) by the modified sol-gel process through oxidative polymerization of thiophene. They reported that polythiophene acts as good sensitizer towards LPG and supporter for the tin-doped titania that improve the photocatalytic activity under visible light.

2.4 Nanocomposites of polythiophene with metal nanoparticles

Bagheri *et al.* [49] synthesized a nanocomposite consisting of polythiophene with a silver (PTh/Ag) by chemical oxidative polymerization in the presence of anhydrous ferric chloride and implemented as a desired sorbent for headspace needle trap extraction. They observed that the presence of Ag NPs within the polymeric structure could be responsible for higher specific surface area and sorption capacity while the PTh moiety contributes to the hydrophobic and π-π interactions. The synthesized nanocomposite was conveniently implemented to the isolation of some selected PAHs from different water samples.

Shanmugapriya *et al.* [50] synthesized the polythiophene (PTh) via *in-situ* chemical polymerization method. Conducting polythiophene (PTh) was blended with micro copper (μ-Cu) and nanocopper doped polythiophene (n-Cu) by mechanical mixing. The room temperature electrical conductivities of PTh, µ-Cu/PTh and n-Cu/PTh were calculated and found to be $7.2x10^{-4}$ Scm^{-1}, $2.8x10^{-3}$ Scm^{-1} and $1.0x10^{-2}$ Scm^{-1} respectively. The result revealed that there is an increase of one order in electrical conductivity in the micro composite and two order of increase in electrical conductivity in the nanocomposite when compared to pristine PTh. The improvement in the electrical conductivity of these composites is expected to enhance the application potential of the polymer composites.

3. Applications of Polythiophene Nanocomposites

Polythiophene nanocomposites have been used for many applications due to their chemical, mechanical, optical and electrical properties. Their semiconductor properties allow conjugated polymers to be used particularly in a large area, such as electrochromic devices (EDCs), rechargeable batteries, light-emitting diodes (LEDs), field-effect transistors (FETs), photovoltaic cells and chemical Sensors.

3.1 Sensors

Kong *et al.* [51] studied the sensitivity test of PTh/SnO_2 composites *viz.* [PTh(1%)/SnO_2, PTh (5%)/SnO_2, PTh(10%)/SnO_2, PTh(20%)/SnO_2 and PTh(30%)/SnO_2] to methanol (MeOH), ethanol (EtOH), acetone and NOx carried out at room temperature, 50°C, 70°C and 90°C. It was found that PTh/SnO_2 composites with different PTh mass percent could exhibit high sensitivity to NOx but no sensitivity to 10 ppm, 50 ppm, 100 ppm, 150 ppm and 200 ppm MeOH, acetone and EtOH. It was also observed that the sensitivity increased with the increase of NOx concentration. It was found that PTP/SnO_2 composites had better selectivity and higher sensitivity than PTh and SnO_2 at much lower working temperature. The PTh/SnO_2 nanocomposites responded to NOx at a concentration as low as 10 ppm. Polythiophene behaved as a *p*-type semiconductor and SnO_2 as an *n*-type semiconductor. So the composites contained the properties of the *p–n* junction.

In another study, Xu *et al.* [32] reported that the gas sensor based on SnO_2 hollow spheres/PTh exhibited higher gas response, good response and shorter recovery time for detecting NO_2 of ppm levels at low temperature than the sensor based on pure PTh. With increasing the NO_2 concentration and PTh contents, the gas response of the hybrids (10%, 20% and 40%) can be improved.

Barkade *et al.* [34] also reported that PTh/SnO_2 hybrid sensors could detect liquefied petroleum gas (LPG) with high sensitivity at room temperature. PTh/SnO_2 hybrid composite containing 20wt% SnO_2 showed the maximum sensitivity at room temperature.

Uygun *et al.* [52] reported that PTh/SiO_2 nanocomposites can be used for the fabrication of novel glucose biosensors with the rapid response time. The amperometric response of enzyme-coated electrodes to glucose was enhanced when the surfactant was present in the preparation of the nanocomposites. The highest linear range from 0.06 to 1.585 mM of glucose was determined for the PTh/SiO_2/Tween-20 electrode. They concluded that the response time of the electrode prepared in the presence of surfactants was from the 30s to 50s while the response time for a surfactant-free PTh/SiO_2 electrode was about 70s.

Huang *et al.* [33] demonstrated that the gas sensor based on the PTh/WO_3 hybrids has a high response and good selectivity for detecting NO_2 of ppm level at low temperature. Both the operating temperature and PTh contents have an influence on the response of PTh/WO_3 hybrids to NO_2. The 10 wt% PTh/WO_3 hybrid showed the highest response at a low operating temperature of 70ºC.

Tripathi *et al.* [53] successfully synthesized Al_2O_3/polythiophene nanocomposites by chemical oxidation polymerization method. They observed the sensing properties of pure and Al_2O_3/PTh nanocomposites at room temperature. It was found that the sensitivity increases with increase in dopant concentration as well as increase in the analyte gas i.e. ammonia concentration. Response and recovery times for these samples have also been measured. The response and recovery time for 8 wt% of Al_2O_3/PTh showed a significant result. The present study suggests that Al_2O_3 doped polythiophene nanocomposites pellets with proper dopant concentration can be used as a sensing material for ammonia.

Bai *et al.* [54] successfully synthesized nanocomposite of ethylenediamine modified-reduced graphene oxide (RGO) and polythiophene (PTh) by *in-situ* chemical polymerization under room temperature for 2 h. They investigated the sensing response of nanocomposites towards NO_2 gas. The response of the hybrid with 5wt% RGO achieves nearly 4 times higher response than that of pure PTh at room temperature. The hybrid is loaded on a flexible PET thin film to structure a smart sensor. The sensor not only exhibits high sensitivity, good selectivity to NO_2 but also has flexible, simple and inexpensive characteristics which will open a new window to develop a kind of portable and wearable electronic devices to detect hazardous gases in the environment.

3.2 Photocatalysis

Zhu *et al.* [55] synthesized PTh/TiO_2 nanocomposite for the photocatalytic degradation of methyl orange (MO) dye under UV light irradiation. They used a self-designed UV-irradiation instrument with 10W germicidal lamps with a maximum wavelength of 253.7 nm for the catalysis process. Absorbance was measured by a UV-vis spectrophotometer that was used to measure the change in the MO concentration. It was observed that nanocomposite absorbs in the wavelength range of 200-800 nm compared to TiO_2 which absorbs only in the 400 nm region. This suggests that the PTh/TiO_2 nanocomposite can be excited by solar light. It was also observed that in addition to the photodegradation phenomenon, the PTh/TiO_2 nanocomposite allows surface adsorption of the dye which changes with the PTh to TiO_2 weight ratio. With the increase in PTh ratio, the adsorption capacity of the PTh/TiO_2 nanocomposites increases first and decreases afterwards which is related to the structural features of the nanocomposite system. When tested under UV light illumination, the pure PTh used as a catalyst did not show any appreciable degradation of MO (< 5.0%). Pure TiO_2

induced 48.5% MO degradation whereas PTh/TiO_2 showed 56.6% degradation. The rate of degradation initially starts at a high pace after which it becomes stable due to the adsorption of dye on the active sites of the catalyst. PTh/TiO_2 with a higher PTh content exhibited limited catalytic activity. This is because PTh adsorbed on the surface of TiO_2 occupied most of the surface-active sites of TiO_2 thereby preventing the MO molecule from reaching the active sites of TiO_2 for degradation. The surface property is an important factor for the photocatalytic properties and is closely related to the PTh to TiO_2 weight ratio.

In another development, Li *et al.* [56] reported that with increasing PTh content from 0 to 2%, the adsorption capacity of the PTh/TiO_2 composites towards MO increases. Zeta-potential studies showed that the surface of the TiO_2 is negatively charged while the surface of the PTh/TiO_2 composites is positively charged in the dispersion. Therefore, MO is barely adsorbed on the TiO_2 surface due to Coulombic repulsion. On the other hand, the positively charged surface of the PTh/TiO_2 composites can adsorb MO strongly which would contribute to the high photodegradation efficiency due to efficient interfacial charge transfer.

Chandra *et al.* [47] also reported that the PTh/TiO_2-Cu composite prepared by a sol-gel process showed a strong interaction between the interface of PTh and TiO_2-Cu. The TiO_2-Cu composite showed absorption in the region, 450- 500nm. On the other hand, an extension of the absorption regions in the PTh/TiO_2-Cu composite also indicates strong interactions between PTh and TiO_2-Cu. It is expected to accelerate photo-induced charge transfer from the PTh to TiO_2-Cu, and subsequent enhancement of the photocatalytic efficiency of the catalyst. When tested for the degradation of rhodamine blue (RhB), the rate of RhB degradation increased as the PTh content in TiO_2-Cu was increased from 0.5 to 2.0 wt.% reaching a maximum at polymer loading of 1.0 wt.%, and decreasing with further increases in polymer loading to 2.0 wt.%. This shows that there is some specific threshold for PTh to exhibit the optimal catalytic properties in the composite system. The experiment also showed that the concentration of PTh in TiO_2-Cu played a significant role in enhancing the photocatalytic activity. The change in pH alters the charge on the catalyst which affects the adsorption and desorption of the dyes on the catalyst surface. For PTh/TiO_2-Cu, the photocatalytic rate also increased with increasing pH.

3.3 Secondary Batteries

Jung *et al.* [57] reported the synthesis of a Ag/poly(3,4-ethylenedioxythiophene) (PEDOT) nanocomposites through polymerizing 3,4-ethylenedioxythiophene (EDOT) and reducing Ag(I) acetate into neutral Ag via a simultaneous one-pot method. It was observed that Ag/PEDOT nanocomposites were formed as a core-shell structure keeping Ag nanoparticles well dispersed in PEDOT polymer with high surface area and high electrical conductivity. They investigated electrochemical characteristics by galvanostatic discharge/charge and cyclic voltammetry (CV). The charge capacity in the initial cycle for Ag/PEDOT nanocomposites showed 291 mAh/g and also that in the 20th cycle was the highest with 209 mAh/g among the other samples. The morphology of Ag/PEDOT nanocomposites makes Li-ions transfer easier and this results in the enhanced electrochemical performance because of sufficient charge transfer in the interface and convenient mass transfer. The discharge-charge properties of the samples were measured at a current density of 0.5 mA/cm^{-2} and a voltage from 0.02 to 2.8 V. The CV of the cell was performed over the voltage range, 0 to 2.8 V, at a scan rate of 0.05 mV/s. Ag/PEDOT core-shell nanocomposites for an anode material were prepared by the one-pot reduction method in order to increase the high surface area. The introduction of PEDOT as a good buffering agent to Ag particles prevents Ag particles from being agglomerated, to improve the dispersion of Ag particles and to make Ag particles more stable.

3.4 Supercapacitors

Melo *et al.* [58] reported that composites of polythiophene (PTh) and graphene (GR) with different mass proportions were studied for their application as supercapacitors. They evaluated the electrochemical behaviour of these composites by means of cyclic voltammetry and specific capacitance curves were derived from these measurements. The Faradaic impedance spectroscopy response of the different composites along with that of GR was also studied. From these measurements, it was found that a 1:1 in a mass composite of GR and PTh showed a higher specific capacitance even when compared with GR alone. The introduction of the GR in that proportion also showed enhanced cyclic stability in comparison with the sole polymer. The high specific capacitance (365 Fg^{-1} at 1 Ag^{-1}) of this composite material indicates its potential for use as an electrode material for supercapacitors. The supercapacitor performances of the resulting materials were tested and compared with each other. The specific capacitance of the best composite can reach 365 Fg^{-1} at a discharge current density of 1 Ag^{-1} which is much larger than the value achieved using pure PTh (92 Fg^{-1}). The mixture when prepared with certain ratios of GR and conducting PTh may open the opportunity to prepare low-cost high-performance electrode materials for supercapacitor applications.

3.5 EMI Shielding

Najar *et al.* [59] successfully prepared nanocomposite of polythiophene (PTh) with the photo-adduct of sodium pentacyanonitrosylferrate(II) dehydrate and hexamine is synthesized by *in-situ* polymerization technique. They reported that dielectric studies showed the dielectric constant of the order of 2×10^{4} at 10^{4} Hz and an AC conductivity of 10^{10} Scm^{-1} of nanocomposite. Due to the high value of dielectric constant and AC conductivity, the nanocomposite can be very useful for EMI shielding applications.

A few review articles on the selective aspects of polythiophene based nanocomposites have also been published [60,61].

Table. 1 Summarized details on preparation and applications the polythiophene based nanocomposites.

S.No.	**Nanocomposites**	**Method of Preparation**	**Applications**	**References**
1.	PTh/Al_2O_3	Chemical/Oxidative	Electrical Conductor	[30]
2.	PTh/TiO_2	Chemical/Oxidative	-	[31]
3.	PTh/SnO_2	Chemical/Oxidative	NO_2 Sensor	[32]
4.	PTh/WO_3	Chemical/Oxidative	NO_2 Sensor	[33]
5.	PTh/SnO_2	Chemical/Oxidative	LPG Sensor	[34]
6.	PTh/Fe_2O_3	Chemical/Oxidative	Sorbent for Solid-Phase Extraction	[35]
7.	PTh/ZnO	Chemical/Oxidative	Photocatalyst	[36]
8.	PTh/SWCNT	Chemical/Oxidative	Conductor	[37,38]
9.	PTh/MWNT	Chemical/Oxidative	Conductor	[39,40,42]
10.	PTh/GO	Interfacial Polymerization	Conductor and Capacitor	[41]
11.	PTh/La-Doped Barium-Ferrite	Chemical/Oxidative	Electrical Conductor	[43]
12.	PTh/Cu-Doped Zinc Oxide	Chemical/Oxidative	Photocatalyst	[44]
13.	PTh/Pd/TiO_2	Chemical/Oxidative	Sensing	[45]
14.	PTh/G/Fe_3O_4	Chemical/Oxidative	Magnetic-Solid Phase-Extraction	[46]
15.	PTh/TiO_2-Cu	Chemical/Oxidative	Photocatalyst	[47]
16.	PTh/Sn-TiO_2	Chemical/Oxidative	Photocatalyst	[48]
17.	PTh/Ag	Chemical/Oxidative	Isolation of Selected PAHs from Water Samples	[49]
18.	PTh/Cu	Chemical/Oxidative	Electrical Conductor	[50]
19.	PTh/SnO_2	Chemical/Oxidative	Sensor	[51]
20.	PTh/SiO_2	Chemical/Oxidative	Glucose Sensor	[52]
21.	PTh/Al_2O_3	Chemical/Oxidative	Ammonia Sensor	[53]
22.	PTh/RGO	Chemical/Oxidative	NO_2 Sensor	[54]
23.	PTh/TiO_2	Chemical/Oxidative	Photocatalyst	[55,56]
24.	PEDOT/Ag	Chemical/Oxidative	Secondary Batteries	[57]
25.	PTh/Graphene	Chemical/Oxidative	Super Capacitor	[58]
26.	PTh/ $Na_2[Fe(CN)_3(OH)(NO)(C_6H_{12}N_4)]H_2O$	Chemical/Oxidative	EMI Shielding	[59]

4. Conclusions and Scope for Future Work

Nanocomposites of PTh show better electrical, mechanical, optical, thermal etc. properties as compared to pure PTh. However, in many cases, the secondary component also tends to reduce its electrical conductivity. In this review, we have summarized the various techniques applied for the preparation of PTh nanocomposites and the fabrication of devices for potential applications including chemical sensor, optical sensors, light-emitting diodes (LEDs), display devices, photovoltaics/solar cells, transistors, rechargeable batteries, supercapacitors, EMI shielding etc. The multi-functionality of PTh nanocomposites have been extensively exploited in diverse applications with impressive results. The synergistic effects between the constituents have made these materials particularly attractive as sensing elements for gases. Efforts are on towards understanding the working mechanism of PTh nanocomposites which will increase their potential fields of applications.

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6. References

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