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REVIEW ARTICLE

A REVIEW ON PROPERTIES AND APPLICATIONS OF CONDUCTING POLYMERS

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ABSTRACT

Conducting polymers (CPs) are very important for the researchers because of their importance in various fields such as economic, environmental and electrical conductivity. These polymers have very important properties such as Optical, mechanical, and electronics. Conducting Polymers shows widest range of applications: such as electrostatic materials, conducting adhesives, electromagnetic shielding against electromagnetic interference (EMI), artificial nerves, aircraft structures, diodes, and transistors. This review papers discuss important potential applications of these nanofibers and nanotubes in various fields such as sensors, nanodiodes, field effect transistors, field emission and electrochromic displays, supercapacitors and energy storage, actuators,

INTRODUCTION

Nanotechnology is the sprightly growing area of research because of its massive potential for a wide variety of applications (1). Nanostructures are classified into four categories namely: 1D, zero-, 2D and 3D structures. These structures are having their own importance but one-dimensional (1D) nanostructures have gained substantial interest because of their aberrant properties such as Physical, electronics, especially on Nano scale systems. 1D-nanostructure have very important feature device function, in different kinds of nano devices (2-4). There has been remarkable breakthrough in 1D-nanostructures with molecular scale and nano scale properties that can meet the demands of society in the modern era. Some examples are carbon nanotubes, inorganic semiconducting etc (5-25). These nano structures have many diverse applications in variegated areas such as nano electronics or molecular electronics, biotechnology, nano composite material, medicine, nano devices. (5-16). These nano-materials possess distinctive properties due to which they have attained special place and can be used as electrical as well as conducting material, used for doping process both reversible doping and dedoping. Polymers such as polyacetylene (PA), polyaniline (PANI), polyfuran (PF), poly (p-phenylene-vinylene) (PPV), poly (3,4-ethylene dioxythiophene) (PEDOT), and other polythiophene (PTh) derivatives, etc., have drawn special attention in the field of nanoscience and nanotechnology because of their These controllable chemical and electrochemical properties and easy processability. (10-15). Different physical and chemical processes have been embraced for the preparation of conducting polymer (CP) nanotubes and nanowires, like electrospinning, template-free method,, hard physical template-guided synthesis and soft chemical template synthesis

(e.g., interfacial polymerization, dilute polymerization, reverse emulsion polymerization, etc.), and a variety of lithography techniques. The following section deals with the specific behavior and working of conducting polymers and their wide range of applications. All the properties of conducting polymers are discussed briefly in this review

CONDUCTING POLYMER: As clear by the name of Conducting polymers. They shows very good conduction properties. A part from these they also show other important properties such as optical properties, electronic behaviour, magnetic, mechanical, wetting, and microwave-absorbing properties Fig. 1

ELECTRICAL-CONDUCTING PROPERTIES: The electrical conducting property of conducting polymers is enhanced by doping. Doping increases their conductivity to a level comparable with metallic conductors. Martin (23) showed that the electrical conductivity of a single nano fiber is one or two orders of magnitude greater than the material in pellet nanotubes or nanowires. Chen and co-workers (24) examined the electrical conductivity of PANI nanotubes; it was observed that the conductivity of a single nano tube was enhanced by two orders of magnitude. Generally, incorporating an insulating component with 1D-conducting polymer nano materials will decrease electrical conductivity because of the partial blockage of conductive path by the insulating component. Long *et al.* (25) showed that the resistivity of beta-naphthalene sulfonic acid (NSA) -doped PANI/Fe₃O₄ composite nano wire pellets increased with decreasing temperature, which is a typical semiconducting behavior. The decreased composite conductivity is attributed to the increased charge carrier scattering between NSA-doped PANI/Fe₃O₄ nanoparticles.

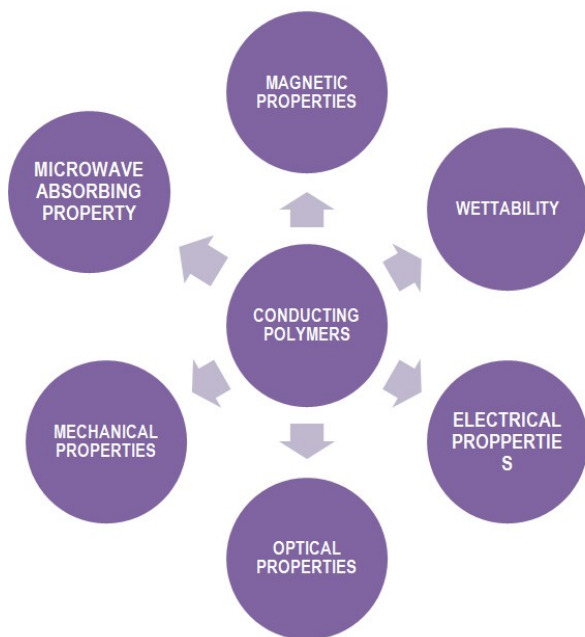


Fig. 1. Properties of Conducting Polymers

A similar decrease in electrical conductivity was also observed in various kinds of 1D-conducting polymer nano composite system (26-28). On the other hand, incorporating another nano component with high electrical conductivity into conducting polymers may enhance the conductivity of nano composites. Long *et al.* (29) studied the electrical conductivities of CNT/ PANI composite nano cables; it was found that the conductivity of pure PANI increases with increasing CNT loading. The CNTs could serve as a “conducting bridge” between conducting domains after their introduction to the conducting polymers, thus enhancing electrical conductivities (30-32).

Furthermore, the conductivity of well-aligned CNT/PANI nano composites decreased with decreasing temperature, indicating a typical semiconductor behavior (33). Similar results have also been obtained for CNT/PPY composite nanocables (34). Incorporation of metal nano particles into conducting polymers can also enhance the electrical conductivity of conducting polymers (35). The electrical conductivity of single Au/PANI nano cables is much higher than a single CSA-doped PANI nano tube (36-37). Various nano structures of functionalized PE DOTs were created using a template-free electropolymerization method on indium-tin-oxide substrate. The result provided the relationship between the functional group, nano structures and electrical properties (38).

MAGNETIC PROPERTIES

Conducting Polymers are magnetically very important as they give information about unpaired spins and charge carrying species (39-42). Lu *et al.* (43) studied the magnetic properties of PANI/Fe₃O₄ composite nanotubes synthesized by an ultrasonic irradiation technique. Long *et al.* studied the magnetic properties of PANI/Fe₃O₄ composites nanorods prepared via a self-assembly technique. Compared to the self-assembly method, the samples synthesized through the ultrasonic irradiation technique facilitate the dispersion of Fe₃O₄ particles. The composite nanotubes synthesized through the ultra sonic irradiation technique showed a super-paramagnetic behavior. The magnetic properties of 1D-conducting polymers/Fe, Co, Ni nano-composites have also been studied (44-47).

OPTICAL PROPERTIES

The unique optical properties of conducting polymers have been extensively explored because of their applicability in nanophotonic devices. The 1D-nanostructured semiconductors are suitable for the fabrication of photodetectors, photochemical sensors, and photonic wire lasers (48-51).

Xi *et al.* (52) studied the optical properties of CdS/PANI composite nanocables and found that the photoluminescence spectrum had similar features to CdS nanowires, but signal intensities were enhanced. Such enhancement was due to the photo-generated carriers transferring from the PANI layer into CdS nanowires. Turac *et al.* synthesized a new polythiophene derivative by electrochemical oxidative polymerization of 2,5-di (thiophen-2-yl) -1- (4- (thiophen-3-yl) phenyl) -1-H-pyrrole (TTPP) and the optical contrast, switching time, k_{max} and band gap have been determined (53).

WETTABILITY

Wettability is one of the most important properties of a solid surface, leading to applications such as self-cleaning surfaces, microfluidics, controlled drug delivery, and bio-separation (54-56). Generally, conducting polymers are hydrophilic (57-58). A film of conducting polymers with super hydrophobic properties can be fabricated by doping hydrophobic acids (59-60). A reversibly switchable super hydrophobic and super hydrophilic surface can be observed by controlling the chemical composition of conducting polymers (61,62). The wettability of films of PAN/PANI coaxial fibers has also been observed to have chemical dual-responsive feature (63). A single-layered photo polymerized nanocomposite film of polystyrene and TiO₂ nano rods change their wetting character from hydrophobic to hydrophilic when deposited on substrates with decreasing hydrophilicity (64).

MECHANICAL PROPERTIES

Recently, the mechanical properties of a single nanotube have drawn much attention (65). Cuenot *et al.* (66) studied the force-curve measurement or resonance-frequency measurement and reported the elastic tensile modulus of polypyrrole nanotube. It was found that the elastic modulus strongly increased when the thickness of the polypyrrole nanotube wall or its outer diameter decreased. Similar size-dependent mechanical behavior has also been observed in other single nanofibers (67-74). Inorganic nanowire such as CuO, silver, lead and nano sized wire.

MICROWAVE ABSORBING PROPERTY

Conducting polymers has also find applications as material absorbing microwave materials due to their lower density and their easy processibility. Wan *et al.* (78) found that PANI-NSA and PANI-NSA/glucose micro-nanotubes prepared by a template-free method show excellent electromagnetic loss. Liu *et al.* (79) reported that the doped polyaniline with fiber-like morphology has a better electromagnetic wave-absorbing property than that of polyaniline with particle-like morphology. Above studies shows that conduction polymers material especially nanotubes can be used as light weight absorbent material with high absorption, wide frequency.

APPLICATIONS OF CONDUCTING POLYMERS

Due to the synergistic effect of multi-components, conducting polymer nano composites exhibit multifunctional and unique properties. Therefore, such conducting polymer nanocomposites are expected to find applications in many fields, such as nano electronic devices, chemical or biological sensors, catalysis or electrocatalysis, energy, microwave absorption and biomedicine

Electronic Nano devices: Most conducting polymers are suited for the construction of electronic devices because of their high electrical conductivity, mechanical flexibility and low cost. Incorporating metals, semiconductors, carbon nanomaterials and insulating polymers into conducting polymers to form nano composites may affect the conductivity of conducting polymers, which is potentially applicable in light emitting diodes, transistors, memory and photovoltaic devices.

Field Effect Transistors and Diodes: Polymer nanofibers are used as Field effect transistors (80-84).

Pinto *et al.* (80) reported an electro-spun polyaniline/poly-ethylene oxide nanofiber field-effect transistor. Liu *et al.* (81) reported a single nanofiber field-effect transistor from electrospun poly (3-hexylthiophene). Qi *et al.* (82) also reported an ultra-short poly (3-hexylthiophene) field-effect transistor with channel length 5–6 nm and width 2nm. Alametal. (83) reported an electrolyte-gated transistor based on conducting polyaniline, polypyrrole and PE DOT nano wire junction arrays. Lee *et al.* (84) also reported an electrolyte-gated conducting polyaniline nanowire field-effect transistor. Guo *et al.* (85,86) analysed that p-n junction nanowire consisting of polypyrrole and CdS fabricated using template of Al_2O_3 . Park *et al.* (87) constructed a nano-device from single Au-polypyrrole-Cd-Au nanorods, which exhibited diode behavior at room temperature. Pinto *et al.* (88,89) reported a Schottky diode using an n-doped Si/ SiO_2 substrate and an electro spun fully doped polyaniline nanofiber. Liu *et al.* (90) demonstrated that Au/template-synthesized polypyrrole nanofiber devices show rectifying behavior and might be used as nano-rectifiers.

Polymer Light-Emitting Diodes, Field-Emission and Electrochromic Displays: Nanofibers/tubes of polyaniline, polypyrrole and PEDOT have also been explored for polymer light-emitting diodes (PLEDs) (91–94), field emission (95–98) and electrochromic displays (99–103). Boroumand *et al.* (93) designed nanoscale of arrays with conjugated-polymer light-emitting diodes. Yan *et al.* (98) & Kim *et al.* (97) reviewed the field-emission cells of template-synthesized PEDOT nanowires. Due to the ability to change color under an applied potential, conducting polymer nanostructures have been investigated as the active layer in electrochromic devices (99–103). For example, Cho *et al.* (99) illustrated fast color-switching electrochromic device established on a nanotubular PEDOT. Kim *et al.* (103) discussed about electrochromic device from nanostructured PEDOT extended on vertical Si nanowires.

Catalysis-Photo & Chemical Catalysis: The catalytic properties of the PANI/Pd composite nanofibers have been studied for use in Suzuki coupling reactions (137). PANI/Pd nanotubes synthesized by the templating method were used as chemical catalysts (138). TiO_2 is very effective photocatalyst, it is strong oxidizing and non-toxic. The TiO_2 catalysis for decomposing toxic inorganic or organic compounds is attributed to the formation of superoxidant (OH^\cdot and $\text{O}_2^{\cdot-}$) generated from water decomposing in the presence of TiO_2 under radiation (139). TiO_2 /PANI bilayer microtubes had an increased catalytic property to decompose methyl orange, which was due to the red shift of the absorption region of TiO_2 because of photosensitization by PANI (140).

Electrocatalysis: Tiwari and Singh have proposed the synthesis of a polymer nanocomposite from PANI/PAA/MWCNTs by an in situ chemical polymerization method. The nanocomposite thus formed has improved catalytic, electrochemical and electrical behavior (141). Huang *et al.* (142) fabricated PANI/ Au composite nanotubes as electrodes for the oxidation of NADH. Zhao and his coworkers fabricated poly (N-isopropyl acrylamide) -grafted multi walled carbon nano tubes on to a PniPAm-modified substrate for bioelectrocatalysis of NADH (143). PPy/Cobalt porphyrin and PANI/Cobalt porphyrin composite nanorods displayed good electrocatalytic properties of oxygen reduction in neutral electrolytes (144).

Energy Storage as Lithium Ion Batteries, Solar Cell & Fuel Cell: Energy has become the most important global concern because fossil fuels are going to be exhausted. Usually, conducting polymer nanostructures have higher specific capacitance values and can be an alternate in the development of the next generation energy storage devices (145–150). Solar cells are energy conversion devices that convert sunlight to electric energy. Conducting polymers have unique properties of light absorbance and hole transporting when combined with metal oxide, which may contribute to the improvement of the photovoltaic efficiencies (151–158). TiO_2 nanotube arrays are considered as good candidates for the construction of solar cells because they provide good pathways for electron migration. Fuel cells convert the chemical energy directly into electricity by

electrochemical reactions. In recent decades, fuel cells have attracted attention for their applications in electric vehicles (159,160). Due to high energy conversion efficiency, fuel portability and environment friendliness, direct methanol fuel cells (DMFCs) have been a research focus in the field of energy applications (161). The effects of an electrocatalyst on the performance of DMFCs have been extensively studied, and conducting polymers with 1D-nanostructures have become good candidates as electrocatalyst supports (162–166). Conventional rechargeable nickel-cadmium or nickel-metal hydride batteries are limited by their capacity and durability. On the other hand, lithium ion batteries that are lighter and have much greater capacity have been considered as the most promising and practical rechargeable batteries (167–171). Thus, the 1D-nanostructured materials have proved to be good candidates in Li-ion battery electrodes because of their high specific capacity and good cycle performance (172–174).

Supercapacitors: Supercapacitors are one of the most promising energy storage devices for a wide range of applications in electric vehicles, uninterruptible power supplies, etc. (175–177) Compared to lithium-ion batteries, supercapacitors exhibit higher specific power. There are mainly three kinds of electrode materials for supercapacitors, i.e., carbon, metal oxides and conducting polymers (178–187). Conducting polymers have high specific capacitance, but their cyclic stability is poor. This drawback has been overcome by the fabrication of conducting polymer nanocomposites (188–193).

SENSORS-Chemical, Optical, Biosensors: Conducting polymers have been widely explored as chemical sensors, optical sensors and biosensors because their electrical and optical properties can be reversibly changed by doping/depoing processes (104–108).

Biosensors: Recently, conducting polymers have attracted much interest in the development of biosensors because they act as excellent materials for immobilization of biomolecules and rapid electron transfer for the fabrication of efficient biosensors (126). PANI/PS composite nanofibers prepared by Electrospinning technique were employed to detect H_2O_2 (127–128). Composite nanofibers containing PANI, Fe_3O_4 and CNTs were prepared and doped with enzyme for the fabrication of glucose biosensors (129). Conducting polymer nanocomposites, when encapsulated with lipase, can be utilized as biosensors to detect triglyceride (130). Shin *et al.* fabricated an amperometric cholesterol biosensor using polyaniline-coated polyester films for the detection of triglycerides (131). Immobilization of DNA onto conducting polymers has been extensively studied for detection of various DNA target sequences and microorganisms (132,133). Zhang *et al.* (134) reported poly (methyl vinyl ether-alt-maleic acid) -doped polyaniline nanotubes for oligonucleotide sensors. Peng *et al.* (135) reported a functionalized polythiophene as an active substrate for a label-free electrochemical genosensor. Langer *et al.* (136) reported a bacterial nano-biodetector, which can also be utilized in bio-alarm systems.

Chemical and Gas Sensors: Gas sensors have a broad range of applications such as industrial production, food processing, environmental monitoring, health care, etc. (109–111) The PANI nanofibers synthesized by interfacial polymerization have shown that they have much higher sensitivity for the detection of NH_3 than conventional PANI films (112). On the other hand, the addition of a second component into 1D-nanostructured conducting polymers can enhance their applications as gas sensors (113). Besides NH_3 , the addition of metal oxide nanoparticles into 1D-nano structured conducting polymers can extend their applications in detecting other gases. For example PANI/ In_2O_3 composite nano fibers synthesized via chemical polymerization were used as sensors in detection of H_2 , CO and NO_2 at room temperature (114). PANI/ WO_3 composite nanofibers were also employed in sensors for detection of H_2 gas; however, the sensitivity was worse than PANI/ In_2O_3 composite nano fiber based sensors (115). Metal salts can also be embodied into the 1D-nanostructured conducting polymer matrix in form of gas sensors. For example PANI/ CuCl_2 composite nanofibers demonstrated a high response for H_2S gas (116). Blend of PANI-PVP has improved

sensitivity towards chloroform and decreased sensitivity towards CH_2Cl_2 (117). The polypyrrole–chitosan layer has been used to detect Zn^{+2} and Ni^{+2} ions in aqueous solution by surface plasmon resonance (118).

Optical Sensors: Gu *et al.* (120,121) demonstrated a single wave-guiding polyaniline/polystyrene nanowire for highly selective optical detection of gas mixtures. Wang *et al.* (122,123) explored the photosensitivity and photo-response of a bunch of polyaniline nanowires, which showed that nanofiber of conducting polymer might be useful in the fabrication of photosensor and photo switch and devices. Zhu *et al.* (124–125) reported a pH sensor of polyaniline perfluoro sebacic acid-coated fabric. PANI/PAA/MWCNTs by an in situ chemical polymerization method. The nanocomposite thus formed has improved catalytic, electrochemical and electrical behavior (141). Huang *et al.* (142) fabricated PANI/ Au composite nanotubes as electrodes for the oxidation of NADH. Zhao and his coworkers fabricated poly (N-isopropyl acrylamide) -grafted multi walled carbon nano tubes on to a PniPAm-modified substrate for bio-electrocatalysis of NADH (143). PPY/Cobalt porphyrin and PANI/Cobalt porphyrin composite nanorods displayed good electrocatalytic properties of oxygen reduction in neutral electrolytes (144).

Microwave Absorption and EMI Shielding: Radio frequency interference/electro-magnetic frequency interference (EMI) is a serious issue caused by rapid proliferation of electronics, wireless systems, navigation, space technology, etc. EMI affects the performance of the electric device as well as various life forms, including human beings. Therefore shielding materials such as metals, carbon materials and conducting polymers have been employed to prevent electromagnetic noise. The uses of conducting polymers as shielding materials have attracted increased attention due to their good electrical conductivity and processibility (194,195). It has been observed that for conducting polymers, when combined with other nano components like CNT, PANI enhances EMI shielding performance (196–198). Polyaniline microtubes/nanofibers (199,200) and polyaniline-multi walled carbon nanotube nano compo-sites (201) can be used as microwave absorbers and electromagnetic interference-shielding materials.

Electro rheological Fluids: Electrorheological (ER) fluids have wide applications in clutch systems, brakes, hydraulic valves, and dampers for their adjustable properties of vibration control under an external stimulus. Particles of high dielectric constant and low conductivity dispersed in a non-conducting fluid medium are generally the component of ER fluids. This property under an electric field can be changed reversibly in a short period of time. Recently, conducting polymers have been mostly used as polarizable particles because of their superior physical properties such as better environmental stability and high polarizability (202–217).

Biomedical Applications: For the past few decades, conducting polymers have drawn much attention for their biomedical applications (218,219). Most biological cells are sensitive to electrical impulses; therefore, conducting polymers can be used in the field of tissue engineering to modulate cellular activities. PANI and PPY are attractive candidates in biomedical applications for their biocompatibility, ease of synthesis, low cost and rich redox chemistry.

Drug Delivery and Protein Purification: To enhance the drug-targeting specificity and decrease systemic drug toxicity, many drug delivery system devices have emerged during the last few decades, which have been used for treatment of different kinds of diseases. The different type of delivery systems include polymeric microspheres, polymer micelles, polymeric nanofibers, micro-nano gels, etc. One of them is the draw backs of the delivery system is to maintain a strict control of ON/ OFF state. To overcome this drawback, conducting polymers have been used as they show a reversible electrochemical response, i.e., they contract upon reduction and expand upon oxidation. Thus, this induced volume change is expected to favor the controlled release of various kinds of drugs (220,221). Various

conducting polymers such as PPY film, PAA microspheres, and PEDOT nanotubes have been used for this purpose (222–224). The controlled drug release based on conducting polymer nanocomposites is a useful means of fabricating electronically active devices with living tissues. Some of the advantages of conducting polymer nanocomposites include: easy loading, little influence on drug activity, and controlled release rate. It has been reported that chemically modified PPY micro tubes can be used as an affinity matrix for protein purification; and, on elution of the protein, the desorption ratio was high (225).

Kim *et al.* (232), to have low impedance and high charge density and a capacity for controlled drug release (233). The biodegradable electrospun nanofiber helps in controlled release of drugs, and the hydrogel layer sustains the release of drugs. The spectroscopy measurements of PEDOT nanotubes have revealed that they can be used as a novel method for biosensing to indicate the transition between acute and chronic response in the brain tissues (234,231). It has also been demonstrated that PPY and PEDOT nanotubes have better adherence to the surface of the electrodes in comparison with their film counterparts (235,236).

Other Applications: One of the potential applications of polyaniline nanofibers is that they are better corrosion protectors for mild steel than conventional aggregated polyaniline (248). Conducting polyaniline nanofibers are used as nanofillers to improve the electrical properties of a ferroelectric copolymer (249). Some of the other potential applications of polyaniline nanofibers, when decorated with gold nanoparticles, exhibit an interesting bi-stable electrical behavior. This behavior allows it to be switched electrically between two states, which maybe used in the fabrication of Plastic digital nonvolatile memory devices.

CONCLUSION

During the last 20 years, magnificent progress has been done in synthesis, morphology, and structural characterizations of conducting polymers. The physical and chemical properties of conducting polymer as well as nanofibers and nanotubes have also been analyzed in detail. The future developments in this field should focus on improving synthetic methods and deriving novel assembly processes for better control of the size, composition, structure, and interface of conducting polymer nanocomposites. The efficient, and large-scale preparation of nanostructures of conducting polymers with non-disperse and well-desire morphology and size, are still in demand. Conducting polymer nanotubes and nanofibers have shown an impressive application potential ranging from energy harvesting and biochemical sensing to electronic devices and drug delivery. However, due to the complicated microstructures of conducting polymers, there are still problems in fulfilling their full potential applications in nanoscale devices, such as the reproducibility and or controllability of individual polymer nanotubes/wires, stability of the doping level, and improving processability of conducting polymer nanostructures. In the area of energy applications, super capacitors based on conducting polymers continue to attract increasing attention for their large specific capacitance. However, their stability is not very good. It is expected that adding another nano component may enhance the stability of the super capacitor device.

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