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Polyindole Based Nanocomposites and their Applications: A Review

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Abstract

Polyindole (PIn) is hetroatomic organic molecule which belongs to the fused-ring family have emerged in the past several decades as promising materials due to their unique physical and electro chemical properties. PIn was successfully synthesized by chemical polymerization of indole. Properties of PIn can be improved by mixing polymer with conducting metals, metal oxide, carbon nano composites and other materials. Polyindole nano composites (PNCs) were characterized through various spectral, thermal and electrical methods. FT-IR (Fourier transform infrared spectroscopy) spectra confirmed the formation of PNCs and SEM (Scanning electron microscopy) reveal the micro structure of surface of PNCs. Thermal characterization revealed that thermal stability of PNCs increases with addition of metal, metal oxide, carbon nano composites and other materials. These studies revealed that PNCs of PIn with other metals have an important influence on super capacitors electro chemical devices, catalysis, anti corrosion, diodes, sensor and biology related applications. This review provide an overview of the preparation of PIn and their composites, followed by their application in various fields with future perspectives.

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Introduction

The escalating population, industrialization and continuous depletion of traditional fuel reservoirs have been serious issues over natural energy production and its storage since last few decades.[1] The demands for production of energy and well regulated system for energy storage is continuously increasing day by day for present and future needs. The source of energy should associate with environmental protection and the prudent replacement of fossil fuels.[2] The conjugated conducting polymers (CCPs) and their PNCs

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have wide applications in the development of research programme and various fields such as communication, pollution, pharmaceuticals, defense and energy storage. The use of CCPs and their PNCs have grown rapidly over past few years. PNCs consist of two components, filler and a polymer matrix. The filler can be an organic material such as carbon, or an inorganic powder of metal. The conductivity, catalytic activity and electro chemical storage depends critically on the characteristics of the filler component.[3] Polyindole (PIn), Polypyrrole (PPy), Polythiophene (PTh) and Polyaniline (PANI) are common examples of CCPs which are used for the development of PNCs. The fabrication of electrodes of PIn with other metal composites are described in the literature below.

PIn Based NCs

PIn has received great attention in past several years because of their good electrical properties, environmental stability and ease of synthesis. PIn may have the properties of both poly (para phenylene) and PPy because indole has both benzene and pyrrole rings. PIn has also high redox activity, good thermal stability, high storage ability and slow rate of degradation in comparison with those of PANI and PPy.[4]

PIn/Metal Composites

Zhou *et al.,* were coated a novel composite catalysts of Pt-PIn on the glassy carbon electrode (GCE) and it used for methanol electro oxidation in 0.5 M H_2SO_4 acidic solution containing 1.0 M methanol. SEM, XRD and the electro chemical technique were used to characterize the fabricated composite catalysts. CV of Pt-based nano composite electrode showed high peak current densities and lower oxidation potential thus efficient catalytic activity.[5]

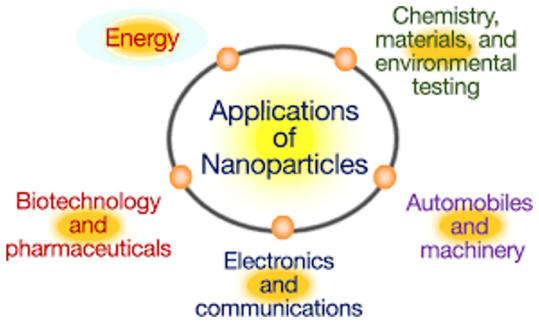

Fig. 1: Applications of Nanoparticles

The development of PNCs comprising PIn and nano sized Au particle via in-situ polymerization of indole, using metal salt chloro-auric acid as an oxidant. The synthesized polymer composite was monitored by UV-visible spectroscopy. The polymerization mechanism of indole and the interaction between PIn matrix and Au nano particles were determined by FT-IR spectroscopy. The XRD confirmed the presence of FCC metallic gold particles in the nano composite. The uniform size distribution and spherical structure of Au nano paticles were reveals by SEM images of nano composite. Further more, the presence of Au was confirmed by EDX and TGA showed the thermal stability of PNCs with respect to pure polymer at a heating rate of 100°C/min.[6]

PIn-Metal Oxides

Trung and Huyen prepared the PNCs of PIn and TiO_2 by chemical polymerization method. FT-IR and Raman Spectra was studied the chemical structure of conducting polymers in PNCs, whereas SEM and TEM was analyze the morphology of PNCs. TGA analysis was carried out at scan rate of 10°C/min in ambient condition which showed that all CPs in the PNCs were stable at more than 600°C. The electrical conductivity of these PNCs was 1.75 Scm^{-1}. The corrosion of PNCs was studied by using electro chemical impedance spectroscopy.[7]

The preparation of PIn-ZnO composite polymer electrolyte (CPE) and its conductivity was studied by Rajasudha *et al.,* The PNC was prepared by chemical method using sodium dodecyl sulphate as stabilizer and anhydrous ammonium peroxydisulphate as oxidizing agent. FT-IR spectroscopy used to studied the formation of PNCs or inter molecular interaction between PIn and ZnO. The surface morphology of PNCs was studied by SEM and TEM image showed incorporation of ZnO in PIn matrix. TGA analyzed the thermal stability of nano composite that increased with adding amount of filler. The ionic conductivity was increased with concentration of ZnO till 50 (%, w/w) and calculated conductivity was found to be 4.405×10^{-7} at 50°C for the CPE from impedance studies.[8] Ganesan *et al.,* synthesized and characterized the CPE of PIn-Fe_2O_3-$LiClO_4$ from different concentration of indole. The impedance spectroscopy was used to analyze ionic conductivity of CPE, which was dependent on concentration of indole.[9]

The synthesis of PIn-SnO_2 composite and its electroc atalytic applications by chemical oxidative method. The characterization of synthesized PNCs through XRD, FT-IR and TEM which confirmed the formation of a uniform nano composite or interaction between polymer matrix and filler. The solution of 0.5 M H_2SO_4 and 1.0 M HCOOH used as electrolyte for the studies of electro chemical technique.[10] Rejani and Beena were synthesize the Mn_2O_3-PIn hybrid structure and then characterized by XRD, FT-IR, and UV-visible. The prepared Mn_2O_3 nano material was in crystalline form and the formation of PNC was confirmed by XRD. UV-visible spectrum studied that the band gap of PIn was decreased with hybrid formation from 4.4 eV- 3.3 eV.[11] PIn and nano-sized magnetite (Fe_3O_4) composite was synthesized by Ramesan. The characterization of PNCs through FTIR, UV-visible, SEM, XRD, DSC and σ DC. The peak of PIn of PNCs shifted towards higher wave number in FT-IR spectra. The Fe_3O_4 nano particles were uniformly dispersed in the polymer matrix and their average sizes were studied by SEM where as XRD reveals the crystalline nature of PIn in which incorporation of Fe_3O_4 nano particles but usually PIn is amorphous in nature. The σ DC depends upon the concentration of PIn and the σ DC of PNCs were higher than pure Pin.[12]

The preparation of PIn-ZnO nano composite was reported by Handore *et al.,* FT-IR spectra confirmed the formation of PNCs at ~3400 cm^{-1} and 735 cm^{-1} band. XRD exhibits major diffraction in between 30-40° that indicates partial crystalline nature of PNCs and SEM revealed agglomerated granular particulate nature with ZnO embedded in the PIn matrix. The calculated conductivity PIn-ZnO nanocomposite was 1.68×10^{-6} Scm^{-1}.[13] The synthesized nanomaterial composite of PIn-Co_3O_4 by in-situ cathodic electro deposition and their structural and morphological changes studied by XRD, SEM, TEM, XPS, FT-IR and Raman spectroscopy. Electro chemical nature of PNCs revealed by CV curves obtained at potential range 0.2-0.5 V in 1.0 M KOH solution. The calculated Cs at a current density of 2 Ag^{-1} is found to be 1805 Fg^{-1}.[14] The nano composite of V_2O_5 and PIn deposited onto the activated carbon cloth for super capacitors. The electrical conductivity of PNC was increased by doping of PIn. CV curve reveals eminent double layer charge storage performance at different S Rs (5-050 mV/s) in 5.0 M $LiNO_3$ solution. The Cs 535.3 Fg^{-1} was reported and these composite showed good cyclic stability with a high rate of 91.1 % after 5000 cycles.[15]

Majumder *et al.,* were improved the electro chemical and stability features of PIn by in corporation of rare earth metal oxides (RE_2O_3 where RE = Nd, Gd and Yb) in PIn matrix. The synthesized PNCs were characterized with the help of FT-IR, XRD, FESEM, TEM and TGA. CV recorded in potential range 0-0.8 V with 1 M H_2SO_4 as electrolyte at a 0.2 Vs^{-1} SR. Cs of PIn was calculated 117 whereas Nd_2O_3 showed higher Cs 401 among the all three rare earth metal oxides.[16] Rekha *et al.,* reported a review on rare earth based conduction polymers that addresses the important examples of rare earth metals and conducting polymers with their synthesis, characterization and application. Studies reveal improved thermal and cyclic stability, with low internal resistance of the composites with application as dielectric, semi conductor and energy storage devices.[17]

Arjomandi *et al.,* synthesized the two novel conducting PIn based Fe_2O_3 and Al_2O_3 nano composite by in situ electro polymerization. The synthesized PNCs were characterized by FT-IR, SEM, TEM, EDX and TGA. The electrochemical properties of PNCs were studied by CV, σDC and EIS. Optical properties was also investigated by UV-visible spectra. TGA analyzed the thermal stability of PNCs were increased as compared to pure PIn. The conductivity of PNCs was increased with concentration of PIn matrix. The electro chemical properties of PNCs were measured at constant current of 0.5 mA/cm^2.[18]

PIn-Carbon NCs

The PIn/c-MWCNT nano composite was synthesized by using in-situ method or interfacial method was studied by Joshi *et al.,* The synthesized PNCs were investigated through different spectral, thermal and micro analytical methods. Electro chemical behaviour studied by using CV at various SR vs. Ag/AgCl in 0.5 M H_2SO_4 and I/V curves of synthesized PNCs were almost linear with a low value of current.[19] A series of PIn-GO nano composite were synthesized through polymerization method, in the presence of different concentration of GO ranging

5-20 (%, w/w) and ferric chloride as an oxidant. The PIn-GO interaction investigated through FT-IR, XRD and SEM. Thermal stability of PNCs were increased with the concentration of GO and CV studied that PNCs of 20% GO showed highest Cs 399.97 in 1.0 M KOH at SR of 0.001 V/s.[20] A high capacitance hybrid PNCs based on RGO and PIn was prepared through chemical oxidative polymerization. The electro chemical properties of prepared PNCs were studied at 1.0 M H_2SO_4 through CV and EIS. The synthesized hybrid nano composite showed Cs of 322.8 Fg^{-1}, good stability with a cycling efficiency of 94.5% after 1000 cycles and high power density of 5000 W kg^{-1}.[21] Oraon *et al.,* fabricated nano clay derived mesoporous CNT-PIn electrode by in situ and ex situ method with the help of layered silicate. The micro structure and formation of nanoclay derived EM was observed by FT-IR, UV-visible spectra, SEM, TEM and XRD. The electro chemical properties of electrode was studied through CV measurements which carried out in the potential range of 0-0.8 V at different SR of 0.01- 0.2 V/s.[22]

The electrically conducting PNCs of PIn with CNT were fabricated by an in-situ chemical oxidative polymerization of indole monomer in the presence of APS as oxidizing agent. Surface morphology was revealed by SEM which showed that CNTs were properly distributed and nano porous structure of PNCs. The measured conductivity of PNC was 0.213 Scm^{-1}, which greater than PIn and I/V characteristic was showed linear graph.[23] Mudila *et al.,* synthesized electro chemical energy storage materials at different concentration (w/w) of graphene ranging from 3-9% with PIn matrix in supercritical CO_2. FT-IR, XRD and SEM investigated the exfoliation of graphene into the matrix of PIn whereas TGA analyzed the thermal stability of PNCs increased with fraction of graphene. The electro chemical behaviour of PNCs was investigated by CV and EIS. PNCs showed Cs of 289.17 Fg^{-1} and power density of 511.95 W/kg with good cyclic stability.[24] The synthesis of PNCs of PIn-RGO with Au nano-material by green and eco-friendly UV radiation method. Using this method, the nano particles of GO and Au were incorporated on the PIn matrix without using any harmful chemical agents. The fabricated nano material showed a low detection limit (0.26 µM) and a good linear range of 0.8-1000 µM.[25]

Miscellaneous PIn NCs

The synthesis of electrically conducting PNCs of polyethylene (PE) with varying concentration of PIn and their characterization was confirmed by FT-IR, UV-visible, SEM and TGA. Electrical σ of PIn and PIn-PE composite was measured in the range of 1.2×10^{-3} to 1.96×10^{-6} Scm-1 respectively at 25°C. PIn was found to be 10-3 times more conducting than composite.[26] Hassanien *et al.,* prepared the conducting PIn nanowires on DNA templated by chemical oxidation of indole using $FeCl_3$ and their formation was confirmed by FT-IR, UV-visible and XPS. At room temperature, the σ of PIn-DNA composites was found to be 2.5-40 Scm^{-1}. Thermal stability of PIn-DNA nano wires revealed by the temperature dependent conductance during two heating/cooling cycles range of 233 to 373 K. The activation energy of 33.5-0.2 $kJmol^{-1}$ was also observed.[27]

PIn and PVC composites were synthesized chemically in the presence of FeCl3 as an initiator. TGA and DSC analyzed the thermal stability where as XRD revealed the amorphous nature of polymer. Conductivity measured the range between 1.0×10^{-5} to 2.1×10^{-4} Scm^{-1} and the σ DC of composite increased with content of PIn (wt, %) or with increasing temperature.[28]PIn-CuS nano composite was synthesized for studied the potential effect of CuS nano particles, morphology and conductiivity. FT-IR confirmed the formation of nano composite and interaction between PIn and CuS. The uniformity and spherical shape of PNCs were showed by SEM images. With increasing the concentration of CuS in PNCs the thermal stability, σ DC and crystallinity were increased.[29] The PIn and bacterial cellulose were prepared the bio degradable conductive composite fiber membrane. The micro structure and composition of fiber membrane characterized using SEM and FT-IR. Conductivity of bacterial cellulose increased with incorporation of PIn up to 4.6×10^{-2} Scm^{-1}.[30]

Conclusion

In this review paper, polyindole based nano composites and their application in energy storage system were introduced. PIn is an electrically conducting polymer that obtained by oxidation of indole at anode in several electrolytes. PNCs were developed by the different composition of electrically

conducting polymer PIn with other different types of nano fillers. These fabricated PNCs have variable electrical conductivity due to different properties of nano fillers. PNCs were characterized by various methods such as FT-IR, UV-visible, SEM, EDX, XRD, TGA etc. The use of CPs and their PNCs have grown rapidly over past few years. These PNCs were utilize in electro chemical energy storage devices.

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Conflict of Interest
The author(s) declare(s) that there is no conflict of interests regarding the publication of this article.

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