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**REVIEW ARTICLE** **OPEN ACCESS**

# A Brief Review of Synthetic Methods and Applications of Polyaniline Nanofibres

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**ABSTRACT**
*The discovery of intrinsically conducting polymers (ICPs) initiated a new arena in research of polymers. ICPs are organic polymers that conduct electricity. ICPs like polypyrrole, polythiophenre, polyacetylenes, and polyaniline have been studied and researched extensively. Conducting polymers emerged as promising materialespecially Polyaniline,unlike inorganic metals and semiconductors, both the synthesis and chemical modification of polyaniline (PANI) offer unlimited possibilities. Polyaniline (PANI) nanofibres have wide applications such as gas sensor, super capacitors, corrosion inhibitors, enzyme immobilizorsetc. This article presents an overview of various preparative methods of PANI nanofibres and its applications.*
***Keywords:*** *Polyaniline (PANI), doping, polymerization, nanofibers.*

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## INTRODUCTION

Similar to the metals and semiconductors, the intrinsically conducting polymers(ICPs) exhibits electrical and optical properties, which makes them the best choice as building components of circuit elements for upcoming nanoelectronic devices[1].Among the all available conducting polymers, Polyaniline is the most promising and well-studied because of properties like its easy synthesis, low cost, better stability, tunable redox and ion-exchange properties. The process ability and conductivity of PANI are also fairly good. Hence, there is ample possibility for modifying the conductivity and processabilty of PANI. Depending on the doping level and in the degree of oxidation Polyaniline exists in various forms which give rise to its interesting potential applications[2].The significance of PANI can be understood from some of the following applications attributed to PANI materials. PANI being electrically conducting in nature can be used for conductive adhesive, conductive ink, conductive paint and electrostatic discharge materials[3-8]. Polyaniline changes its color on change in the pH of the medium due to the process of protonation-deprotonation which gives rise to its use as acid-base indicator[9].Morphology of PANI gets affected due toprotonation-deprotonation andoxidation-reduction processes which are useful in membranes for gas separations[10].Polyaniline can be transformed from highly conducting to almost insulating material which gives rise to its use as a digital memory device[11].Its ability to change its electron-donating orelectron-accepting properties can be successfully employed in p-n heterojunctions, diode, solar cell etc.[12-14]. PANI emits color under various excitations, which gives rise its use as organic or polymer light emitting diode[15]. Its ability to accumulate and transform energy which gives rise to its use as electrode for rechargeable batteries, anode for microbial fuel cell[16,17].Now a day's researchers are looking for changing the physical properties of PANI by adopting the different synthetic routes. Especially, nano PANI material are proved to be of great synthetic significance for their useful and tunable properties. We have presented in this article some of the preparative methods of PANI nanofibres and applications regarding them.

## SYNTHETIC METHODS FOR PANI NANOFIBRES

### *a) General methods of PANI synthesis*

PANI has been synthesized by various methods such as chemical oxidative method, electrochemical, template, plasma, enzymatic, photo, and a number of other special methods. Chemical method of polymerization can be subdivided into various different methods like heterophase, solution, metathesis, seeding, self-assembling, interfacial, and sonochemical polymerization. There are methods such as the conventional chemical-polymerization, galvanostatic, potentiostatic and potentio-dynamic electropolymerization processes in an aqueous acid. These methods have been extensively used for the preparation of PANI thin films.

### *b) Importance of synthesis of PANI nanofibres*

In recent years, Polyaniline nanofibres have been studied extensively by researchers, since such materials possess the advantages of both low-dimensional systems and organic conductors. Nanaofibres are in the range of less than 100 nm. The small diameter of the nanofibresis responsible for high surface area within the film. This property can be employed in applications like gas sensors and supercapacitors. For instance, the porous nature of the nanofibrefilms, which permits gaseous phase to diffuse in and out of the fibers rapidly.

### *c) Some salient methods for synthesis of PANI nanofibres*

Recently many authors have reported the synthesis of PANI nanofibres. Conventional oxidative polymerization approaches include the use of insoluble solid templates such as opals, zeolites and controlled pore size membranes. Templates and surfactants also play an important role in the synthesis of PANI nanofibres. M. C. Arenas *et al*. synthesized PANI nanofibres by oxidative polymerization of aniline in presence of binary dopant agents HCl-Poly acrylic acid, HCl-2-acrylamido-2-methyl-1-propanesulfonic acid and HCl-sodium dodecyl sulfate solution. The use of binary doping agents transforms the dimensions and morphology of nanofibres improving the conductivity [18]. A. Sadek *et al.* deposited the doped and dedoped PANI nanofibres onto conductometric sapphire transducers using chemical oxidative polymerisation of aniline in presence of HCl as a dopant [19].B. Kavitha *et al.* synthesized Polyaniline nanofibres by polymerization of aniline in presence of HCl as catalyst and ammonium peroxidisulphate as oxidant by chemical oxidative polymerization method[20]. A. Rahy et al. carried out the polymerization of aniline using 1M HCl, ammoniumpersulfate (APS) with additional use of sodium hypochlorite solution as a co-oxidant. In this new method, PANI nanofibres of several micrometers in length with less than 40 nm diameter are produced with narrower molecular weight distributions. They showed good electrical conductivity as high as 24.4 S/cm calculated by four probe methodtechnique [21]. Surwade and co-workers invented a one-step synthesis of bulk quantities of PANI nanofibres and oligoanilines of controlled molecular weight using $H_2O_2$ oxidant. This synthesis is achieved without added catalysts[22]. The influence of supporting the potential of electropolymerization, electrolyte concentration, the growth time, and the monomer concentration on morphology of PANI nanowires were studied by Yanyan Cao and his team. They synthesized the Polyaniline nanowires electrochemically in aqueous $H_2SO_4$ solutions. During growth, increase in $H_2SO_4$ concentration induces a transition from solid nanowires with tubular ends to open nanowires [23].It is also fascinating to note that the chiral Polyaniline nanaofibres can be synthesized successfully. They found some potential applications in surface-modified electrodes, separation of chiralas well as chemical and biological sensors. W. Li *et al*. synthesized Chiral Polyaniline (PANI) nanofibres by polymerizing aniline in the presence of a chiral acid. The synthesized chiral PANI nanofibers which exhibited extremely high surface area [24].

Nanofibres can be also synthesized by interfacial polymerization method which can be considered as an alternative method to bulk polymerization. It involves two immiscible solvents with one monomer in one solvent and other monomer in another solvent as shown in Figure 1.J. Huang etal. reported a chemical method to prepare high quality PANI nanofibres of identical diameters between 30 and 50 nm with lengths changing from 500 nm to several micrometers, using aqueous/organic interfacial polymerization[25]. The morphology of PANI polymer prepared by means of interfacial polymerization process offers very fascinating morphological features. In an attempt to synthesize nanofibres of conducting Polyaniline by rapid liquid-liquid interfacial polymerization method, M. Kulkarni and coworkers used ammonium persulphate as an oxidizing agent[26].

Out of various physical methods available, "seeding" method is a one-step synthesis for PANI nanofibres without the need for surfactants, large organic dopants, and/or large amounts of insoluble templates. X. Zhang *et al*. synthesized the bulk quantities of nanofibres of increased capacitance values by this method [27]. Synthesis of PANI composites is proved to be another method for the effective utilization of any form of PANI (infusible, insoluble). PANI composites can be used as conductive filler in a suitable insulating matrix. The advantages of composites are that they can be processed in effective way, exhibit better mechanical properties and have numerous applications. G. Ling Teoh *et a*. prepared conducting

polyaniline-$Al_2O_3$ composite nanofibres of diameters of 37–52 nm and lengths of up to μm, with varying conductivity by the method of seeding with $Al_2O_3$nanofibres and oxidative polymerization of aniline [28]. Physical methods such as electrospinning, wet spinning etc. can also beemployed effectively for the synthesis of PANI nanofibres. Electrospinning is a well-known method to polymer nanofibres production. This method offers large-scale production of meters-long fibers for inclusion into smart textiles and wearable electronics. Electrospinning can generate fibers as small as 100 nm. Following literature reveals the use of this intriguing method. V. Jagadeesh Babu *et al* used PANI salts as fillers in PMMA matrix and nanocomposite fibers were obtained by electrospinning [29]. Y.Zhou *et al* fabricated electrospun nanofibres of doped polyaniline/polyethylene oxide blend with diameters smaller than 100 nm. They observed certain pattern of behavior in the electronic properties of polymer nanofibres. The I –V characteristics of single fibers give a lower bound on the bulk conductivity of 1022 S/cm for 70 nm diameter fibers and 1023 S/cm for 20 nm diameter samples [30]. A. Mirmohseni et al. prepared conducting fibers of PANI/nylon 6 blend by wet spinning technique from concentrated formic acid [31].

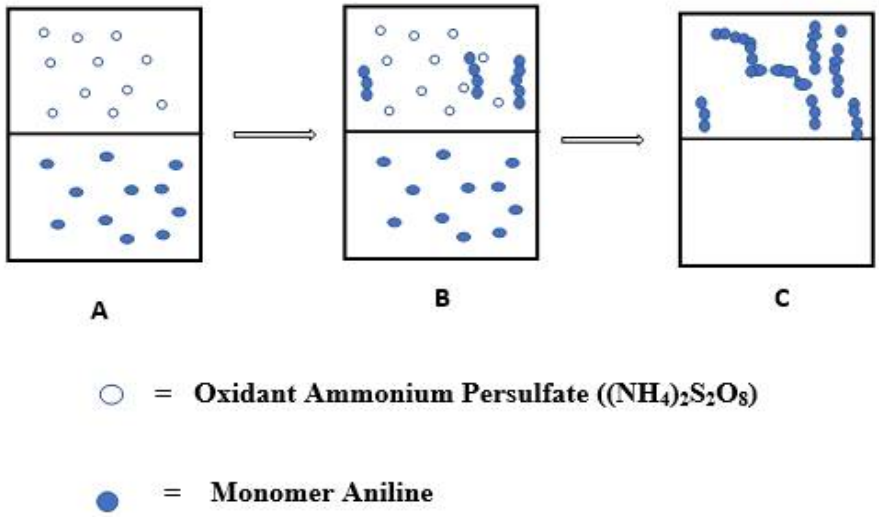


**Figure 1: Interfacial Polymerization for synthesis of PANI Nanofibres**

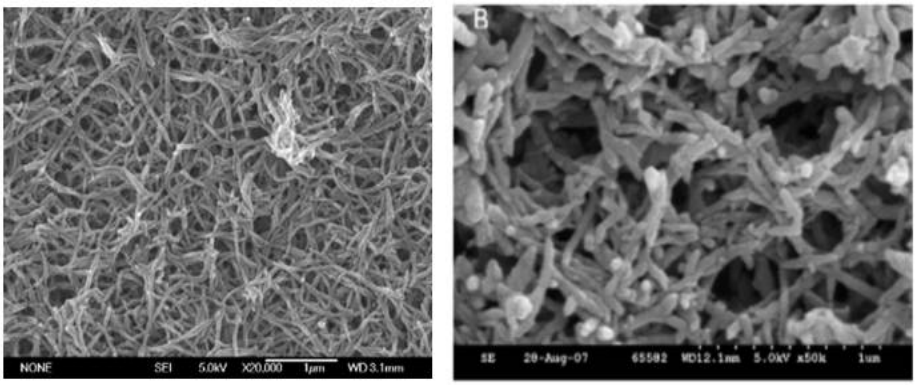


**Figure 2: SEM imagesof PANI nanofibers [Ref. (39), (40)].**

PANI nanofibres can also be synthesized by simple electrodeposition technique. G. Li etal. invented a method for controlled electro deposition of Polyaniline from colloidal suspensions, which are formed by dispersing polyaniline/formic acid solution into acetonitrile [32].D.S. Dhawale etal. electrodeposited Polyaniline nanofibres from a solution containing 0.2 $MH_2SO_4$ + 0.2 M aniline ($C_6H_5NH_2$) at room temperature (300 K) in potentiostatic mode by applying a constant potential of +0.75 V/SCE for the deposition period 420 s[33]. G. Umadevi *et al* electrochemically synthesized Polyaniline by varying at DC voltages from 1.1 V to 2.1 V which gave more pure form of Polyaniline than that of the chemically synthesized. At 1.7 V, the conductivity was well exhibited by HCl doped PANI which showed that the applied DC voltage plays a role on the synthesis of Polyaniline using HCl[34]. R. Pauliukaite *et al.* prepared PANI fiber microelectrodes from a doped solution of Polyaniline protonated with 2-acrylamido-

2-methyl-1-propanesulphonic acid in dichloracetic acid exhibits good conductivity in solutions of high acidity (pH ≤1) [35].

## APPLICATIONS OF PANI NANOFIBRES

### *a) As supercapacitors*

Supercapacitors basically work on same principle as the conventional capacitors, but consist of electrodes of high surface area and thin dielectrics to decrease separation between the electrodes, to increase both capacitance and energy. Supercapacitors provides high discharge currents, recharges fastly, have long service life, no maintenance and highly efficient.S. H. Kazemi et al. studied Metal-Polyaniline nanofibre composite for supercapacitor applications. They found the potential application of the composites to use as electrode materials for supercapacitor. Higher specific capacitance in addition to good cycle stability was found for the metal-PANI nanofibres[36]. Using electrochemical study, Dhawale et al. showed that the Polyaniline electrode exhibited high stability with specific capacitance of 861 F $g^{-1}$ at 10 mV/s scan rate[33].

### *b) As gas sensors*

Compared to conventional, agglomerated Polyaniline that forms non-uniform films, the nanofibres have additional advantages natural to nanoscale materials viz. a porous structure and a large surface-to-volume ratio. These properties result in fast and effective sensors.PANI nanofibres also offer sensitivity with parts per billion detection limits, excellent reversibility for base sensing, fast response times, low fabrication cost, and robustness. R. Arsat et al. developed $H_2$ gas sensors based on highly ordered PANI nanofibres[37]. P. Stamenov et al. found that the acid doped PANI nanofibrous thin films showed faster response to ammonia gas [38]. A. Sadek and co-workers fabricated the surface acoustic wave sensors based on PANI nanofibres, which exhibited remarkable fast response and recovery time for $H_2$ gas [19]. Surwade et al. found that PANI nanofibres are suitable to detect $NO_2$ vapors [22].

### *c) As corrosion inhibitors*

Polyaniline can be succsefully used as corrosion inhibitor. PANI nanofibers synthesized by interfacial polymerization method are proved to be having good dispersion stability in solvent like ethanol. It can form even and compact layer of coating on the carbon steel. It is found that the carbon steel coated with PANI nanofibers has shown excellent corrosion protection than that with aggregated PANI [41].Self-doped sulfonated polyaniline (SPANI) nanofibers synthesized by a rapid mixing polymerization process is appropriate corrosion inhibitor for waterborne layer due to its very small nanofiber morphology, excellent water solubility and distinctive reversible redox pattern. Nonetheless, due to the poor quality linkage of PANI coating to metal substrate restricted its practical application, blending the PANI nanofiber in the polymer resin as astabilizeris good choice for the adhesion of organic coating and electroactive properties of PANI[42].

Yunyan Zhao and co-workers used electrospun PANI/PMMA (Polymethyl Methacrylate) nanofibers and employed as anticorrosion coatings for carbon steel. The maximum anti corrosion efficiency which is found to be about 500 times greater than that from traditional drop casting PANI/PMMA coating could be achieved for the e-spun PANI/PMMA coating as 99.99%. Even the obtained nanofiber was immersed in 0.1 M $H_2SO_4$solution for 20 days, 99.96% as corrosion protection efficiency was attained[43]. These results leads to the development in low cost-effective anticorrosion coatings.

### *d)As enzyme immobilizor*

PANI nanofibers can be used as immobilization matrices which show better properties than other carrier materials, such as ease of preparation, their environmental stability direct electron transfer ability between an enzyme and a polymer, higher enzyme loading per unit mass with less diffusion resistance with higher conductivity and more superficial fabrication. The asparaginase enzyme can be immobilized by PANI nanofibers which exhibit properties like enhanced activity, reusability, sustainability. Moreover, these immobilized nanofibers are more steady towards decomposition/denaturation with changing pH and temperature as compared to the free enzyme [44]. Linking of biomolecules to polyaniline nanostructures is useful as bio-active functionalities are fixed to a redox active nano-dimensional structures. Some of the advantages of the nanostructured form of PANI are very large surface-to-volume ratio thus enabling the immobilizations of a higher number of biomolecules, and an improvement of sensor sensitivity and response times. Adsorption is the method by which immobilization of biomolecules can be obtained by electrochemical or physical techniques. However, using adsorption as the technique of immobilization, has the drawback that there is possibility of desorption of biomolecules from the surface during use. Instead, covalent attachment of biomolecules to surfaces of nanomaterial confirms adequate immobilization without leakage of the biomolecules from the substrate surface during use [45]. Carol Crean *et.al*. demonstrated the use of polyaniline nanofibers as templates for the covalent immobilization

of biomolecules. They functionalized polyaniline nanofibers post-polymerization to attach either amide or carboxylic acid side-groups [40].

## CONCLUSION

This paper discusses various different methods available for synthesis of PANI nanofibers such as oxidative polymerization, interfacial polymerization, electrochemical polymerization, electrospinning, electrodeposition etc. The morphology of PANI nanofibers could be influenced by these methods which in turn could affect the properties and applications of PANI nanofibers. The significance of PANI nanofibers can be understood from their potential applications in gas sensors, supercapacitors, corrosion inhibitors and enzyme immobilizer.

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