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Surface-modified polyacrylonitrile nanofibers as supports

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Abstract

Polyacrylonitrile nanofibers (PAN-nfs) are one of the most studied nanofibres because of their excellent characteristics, such as good mechanical strength, chemical resistance, and good thermal stability. Due to the easy dissolution in polar organic solvents, PAN-nfs are mostly produced via electrospinning technique. The electrospun PAN-nfs surfaces are relatively in-active and hydrophobic, and, therefore, hinder some potential applications; however, chemical surface modification reactions, such as amination, reduction, hydrolysis, and amidoximation, have been carried out on them. These reactions bring about functional groups, such as amine, hydroxyl, carboxylic, imine etc, to the surface PAN-nfs and invariably make their surfaces active and hydrophilic. The surface-modified PAN-nfs have been used as supports for organic compounds, enzymes, and antibodies in biological studies. They have also been used for immobilization of various organic ligands for adsorption of metal ions in water. Furthermore, because of their ability to complex metal ions, several surface-modified PAN-nfs have also been used as supports for transition metal catalysts in Fenton's chemistry.

Introduction

All chemical surface modifications are often used to prepare (activate) PAN-nfs surfaces for immobilization of materials, such as organic ligands, enzymes, antibacterial agents, and catalysts. Covalent binding of these materials is always emphasized for the sake of reusability and to eliminate concerns regarding adverse effects that may be associated with leaching of any of these materials [1]. Tethering of enzymes or antibacterial agents to solid supports via functional groups can give characteristics, such as specific absorption, greater stability, and enhanced biological activities [1, 2]. Surface-modified PAN-nfs have extensively been used as supports for different enzymes for various industrial and biomedical applications, such as biocatalysts, bioreactors, and protein filtration [3, 4]. PAN nanofibres have a relatively hydrophobic surface; therefore, the driving force for protein adsorption is generally attributed to the hydrophobicity [3–5]. PAN hollow fibres have also been used as dialyzers that enable low-to-middle molecule protein (urea, macroglobulin) removals and high-flux dialysis therapy [6, 7]. Commercial examples of such fibres is produced by “Hospal”, a brand of Gambro in the USA, fabricated from an acrylonitrile/methallyl sulphonate copolymer. PAN nanofibres and its composites have been widely used for adsorption and found to be efficient for removal of metal ions and

organic pollutants from water [8–13]. Pendant amines immobilized on PAN-nfs have been used for removal and recovery of metal ions [9–11, 13]. In the same vein, transition metal catalysts have been immobilized on various surface-modified PAN-nfs for use especially in Fenton's chemistry [14–16]. Having highlighted all these, it is, therefore, imperative to bring together various ways chemically modified PAN-nfs that can be used as support for materials. This review critically looked into the various ways of using chemically modified PAN-nfs have used as supports. The chemical modification will be discussed using characterization techniques such as attenuated total reflectance-fourier transform infra red (ATR-FT-IR) and scanning electron microscope (SEM) results.

Pendant-amine-modified PAN-nfs as supports

PAN-nfs have been reported as a suitable starting material for preparation of heterogeneous catalysts based on fabric materials [17–19]. Xu et al. [17] prepared a novel tertiary aminated fibre catalyst based on PAN-nfs. The fibre was efficiently used to catalyze tandem Michaelis-intramolecular Henry reactions between 1,4-dithiane-2,5-diol and *trans-b*-nitrostyrenes to form the corresponding tetrahydrothiophene derivatives. The fibre catalyst exhibited excellent recyclability and reusability up to ten times with only a slight loss in catalytic activity.

The preparation of the tertiary amine immobilized fibre catalyst (PANTF) was carried out via a two-step process. The first was amination PAN-nfs. PAN-nfs was added to ethylenediamine (20 mL) and water (40 mL) in a three-necked flask. The mixture was stirred and refluxed for 3 h; afterwards, the aminated-PAN-nfs (APAN-nfs) was removed, washed, and dried. The weight gain of APAN-nfs was 12.8 % as calculated according to Neghlani et al. [9]. Xu et al. [17] explained that there were some cross-linking reactions induced by ethylenediamine on PAN-nfs. The second step was the tertiary amine immobilization process. The APAN-nfs was reacted with the tertiary amine at optimal conditions of APAN-nfs to NaHCO₃ to 3-dimethylaminopropylchloride hydrochloride mole ratio of 1:3:4 with stirring and reflux for 180 min. The resultant PANTF had a weight gain of 13.0 %. Synthesis of tertiary amine catalyst from PAN-nfs and triethylenetetramine has also been reported in this manner by Li et al. [18].

Zhang et al. [20] have also synthesized a novel halochromic fibre by first aminating commercially available polyacrylonitrile fibre with ethylenediamine and then immobilized phenolphthalein covalently through a mannich reaction. After amination of PAN-nfs with ethylenediamine [17], the dried APAN-nfs was reacted with phenolphthalein in 40 % aqueous formaldehyde (10 mL) and ethanol (30 mL) in a three-necked flask. The mixture was stirred and refluxed for 12 h under nitrogen environment. Afterwards, the mixture was cooled; the fibre was filtered out and washed with ethanol. Then, the fibre was extracted over more than 36 h by methanol with Soxhlet's apparatus to remove any residual small molecules and then dried at 70 °C under vacuum overnight to yield the halochromic fibre with a weight gain of 11.4 %. This halochromic fibre exhibited remarkable colour change from pale yellow to violet in a wide range of alkaline solutions (pH [10.1) with short response time (300 times) [20]. The SEM images of the surfaces of the PAN-nfs after

amination and halochromic PAN-nfs are still rather smooth, which indicates that the fibre retains enough physical durability to meet the needs of its application [20].

Xu et al. [17] reported the FTIR spectra of PAN-nfs (Fig. 1a) and tertiary amine immobilized PAN-nfs (Fig. 1b–e). After amination, there is a broad band ranging from 3700 to 3150 cm^{-1} in APAN-nfs spectrum (Fig. 1b), which corresponds to the stretching vibrations of N–H. The great decrease in the C–O peak (1731 cm^{-1}) and the slight decrease in the CN (2241 cm^{-1}) peak imply that some of the CN groups were modified by ethylenediamine and that the ester groups reacted preferentially with the ethylenediamine [17].

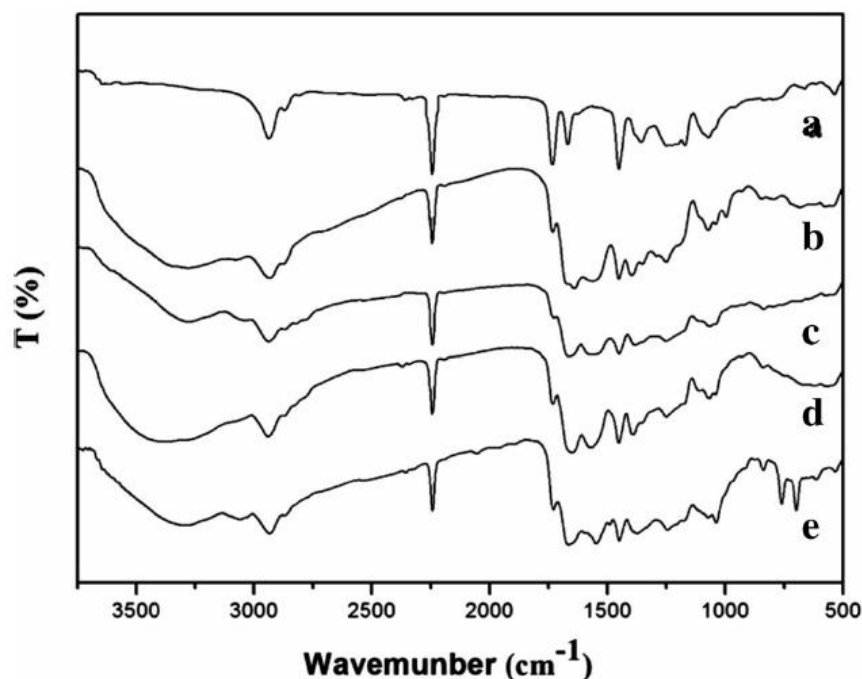


Fig. 1 FTIR spectra of **a** PAN-nfs, **b** APAN-nfs, **c** tertiary amine PAN-nfs, and **d, e** reusability of PANTF Xu et al. [17]

In the catalyst-modified fibres, the strong band at 1650 cm^{-1} is attributed to the amide I band and the new peak at 1560 cm^{-1} is the overlap of the amide II band (Fig. 1c). Figure 1d, e is almost the same as that of Fig. 1c. This indicates that the functional groups on the fibre catalyst still exist after being reused ten times [17].

Moreover, Zhang et al. [20] in their work showed the broad peak at 3700–3150 cm^{-1} is red-shifted and intensified, which illustrate the existence of the O–H groups in the hydroxymethyl of the immobilized phenolphthalein moieties. The 1731 cm^{-1} C=O stretching vibration peak of phenolphthalein immobilized PAN-nfs increases compared with that of APAN-

nfs which is attributed to the introduction of the lactone group in the immobilized phenolphthalein. In addition, the peak at 1560 cm^{-1} decreases significantly as compared to that of APAN-nfs spectrum, which agrees with the reactive consumption of the amino groups [20]. In summary, the FT-IR peaks explained above are suggesting the successful use of PAN-nfs as support.

Hydrazine-modified PAN-nfs as supports

Wen et al. [21] immobilized 8-Hydroxyquinoline on polyacrylonitrile hollow fibre membrane for the preconcentration of rare-earth elements (REEs). PAN-nfs was first reacted with hydrazine, and the HZPAN-nfs was soaked in a 400 ml solution of 20 g of NaNO_2 in 0.2 M acetic acid for 1 h at $0\text{ }^\circ\text{C}$. The product was filtered and rinsed with ice-cold doubly distilled deionized water and then added to a 50 ml solution of 1 g of 8-hydroxyquinoline in 95 % ethanol. After 1 h reaction, the pink diazo-coupled 8-hydroxyquinoline product was filtered and rinsed sequentially with 500 ml 0.5 M NaOH, 500 ml H_2O , 500 ml 1.0 M HCl, and three portions of 500 ml doubly deionized distilled water. The ligand immobilized PAN-nfs was then soaked in deionized distilled water washed and dried before use. The functionalized fibre was stable in treatment 1.0 M HCl, 0.1 M HNO_3 , and 0.5 M NaOH for 2–48 h. In addition, it should be pointed out that after 48 h of exposure, the colour of the 8-hydroxyquinoline immobilized PAN-nfs was changed to yellowish orange. This may be due to the hydrolysis of nitrile groups, leading to the formation of carboxyl groups [21, 22]. This same procedure for immobilization of 8-hydroxyquinoline was also reported by Wen and Shan [22] with a slight change. The HZPAN-nfs was first aminated by reaction with 400 mL of 50 % v/v diethylenetriamine for 6 h at $95\text{ }^\circ\text{C}$ in waterbath. The product was removed and washed with ethanol (99.5 %) and then with double-distilled deionized water until the pH was neutral. Then, the fibre was reacted with NaNO_2 before being immersed in ethanolic 8-hydroxyquinoline to produce the red–brown 8-hydroxyquinoline-modified PAN-nfs.

Reduced PAN-nfs as supports

Jain et al. [1] reduced PAN-nfs with LiAlH_4 (Fig. 2a) to amino groups and activated it with glutaraldehyde for the covalent linking of Goat anti-Rabbit enzyme conjugate. After the reduction process, the primary amine groups of the reduced PAN-nfs had reacted with one of the aldehydic groups of the bi-functional glutaraldehyde to form the imine linkage (Fig. 2b).

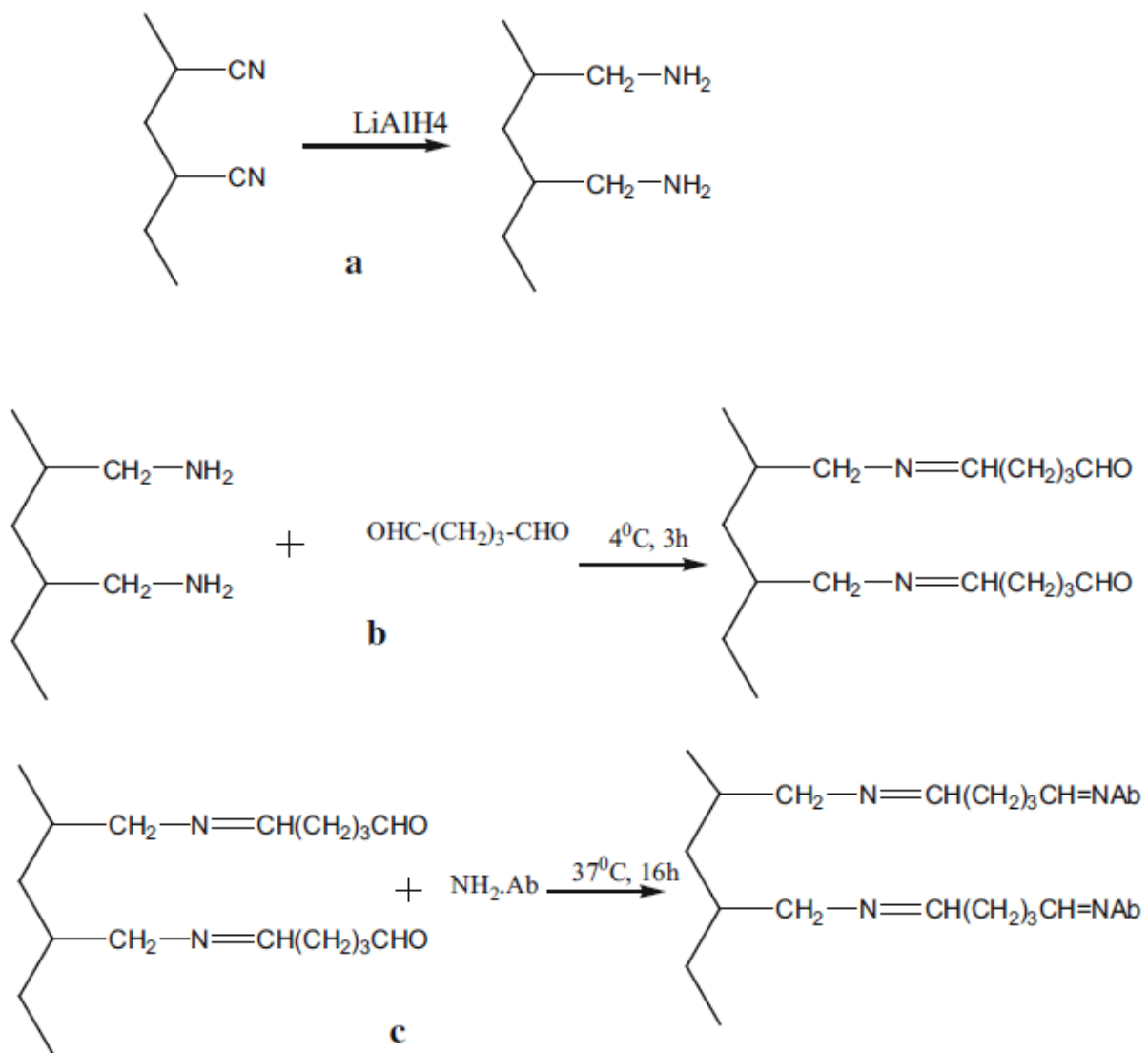


Fig. 2 Reaction of (a) reduction of nitrile, (b) PAN-nf-NH₂ with GA, and (c) GA-activated PAN-nf-NH₂ with antibodies

Then, the PAN-nfs was used for the covalent linking of Goat anti-Rabbit enzyme conjugate. The authors explained that the free aldehyde group of glutaraldehyde (GA) (Fig. 2b) covalently bonded to the amino groups of residues/units (generally lysine) in the antibodies coupled with enzymes (Fig. 2c); therefore, the antibodies were covalently immobilized on the glutaraldehyde-activated PAN-nfs.

Leiriao et al. [23] also introduce primary amine to the surface of PAN-nfs for covalent binding of horseradish peroxidase (HRP) using GA in the presence of a soluble carbodiimide. Ishimura et al. [24] reduced the PAN-nfs with LiAlH_4 and immobilized penicillin acylase on them to study the activity of the enzyme after the attachment on the PAN-nf-NH₂ in terms of specific activity and immobilization yields. Mei et al. [2] reported the successful immobilization of polyhexamethyleneguanidine hydrochloride (PHGH) using lyceroldiglycidylether (GDGE) and poly(ethylene glycol)diglycidyl ether (PEGDGE) as

hydrophilic flexible spacers on the surface of reduced PAN-nfs. The hydrophilic flexible linkers on the surface of the fibre did not only serve as spacers, but also displayed cell-resistant properties by removing attached dead cells [2]. Mei et al. [2] demonstrated the immobilization of PHGH on PAN-nfs by EDX analyses (Table 1). After introduction of hydrophilic flexible spacers (GDGE and PEGDGE), the atom percentage of oxygen increased significantly, while the nitrogen concentration decreased. Following PHGH conjugation, the nitrogen concentration increased, while the oxygen concentration decreased. These changes are to be expected on the basis of the composition of the chemical reagents [2].

The surface morphology as observed on SEM images by Jain et al. [1] noted that no major morphological changes happened on glutaraldehyde-activated PAN-nfs. After immobilization of antibodies, it was observed at higher magnification that the antibodies deposited on the surface of the fibres [1]. Considering this deposition, one would expect a leaching study to be carried out; however, the author did not present any results on leaching.

ATR-FT-IR was also used to monitor the functionalization and immobilization. Mei et al. [2] (Fig. 3a, c) reported the peak at 1080 cm^{-1} and assigned it to CO–C stretching vibration which indicates the presence of the flexible spacers.

Table 1 Surface elemental composition (atom percentage) various modified PAN-nfs Mei et al. [2]

Samples	C (atomic %)	N (atomic %)	O (atomic %)
PAN-nfs	82.27	13.60	4.13
PAN-nfs-NH ₂	86.68	13.30	4.02
PAN-nfs-NH ₂ -GDGE	81.12	12.56	6.32
PAN-nfs-NH ₂ -PEGDGE	81.48	12.45	6.08
PAN-nfs-NH ₂ -GDGE-PHGH	81.88	13.44	3.68
PAN-nfs-NH ₂ -PEGDGE-PHGH	82.57	13.10	4.33

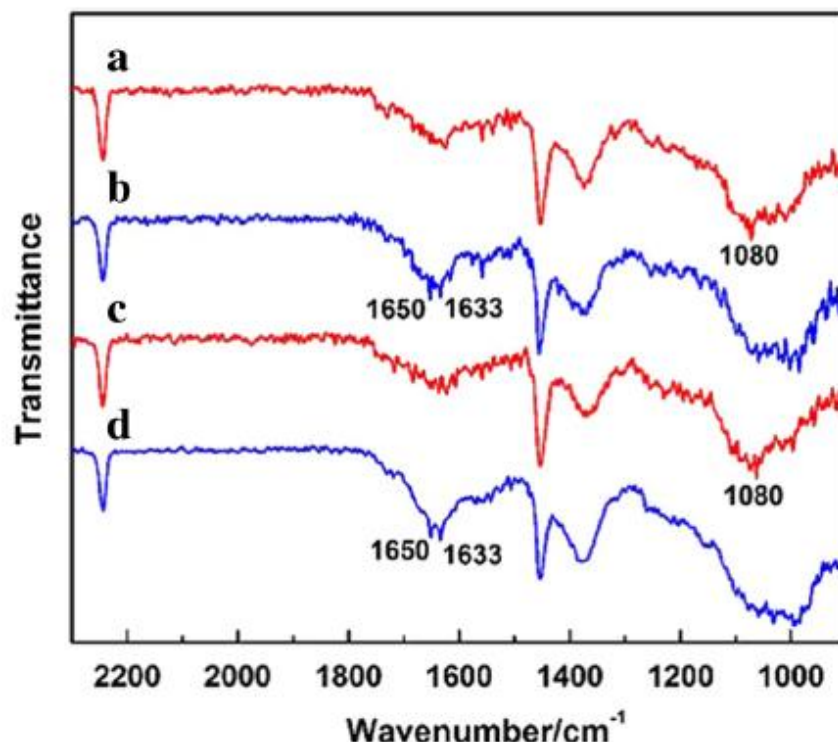


Fig. 3 FTIR spectra of *a* PAN-nfs-NH₂-GDGE, *b* PAN-nfs-NH₂-GDGE-PHG, *c* PAN-nfs-NH₂-PEGDGE, and *d* PAN-nfs-NH₂-PEGDGE-PHG Mei et al. [2]

The amine in-plane bending vibration and imine stretching vibration peaks at 1633 and 1650 cm⁻¹ of the attached PHGH were also observed, thus confirming the immobilization (Fig. 3b, d). Jain et al. [1] also observed a peak at 1655 cm⁻¹ which corresponds to stretching vibration of imines group of glutaraldehyde. However, the peak of free carbonyl group of glutaraldehyde at 1730 cm⁻¹ was not pronounced, as it is merged with that of the carbonyl peak of methacrylate on PAN-nfs. The spectrum of antibody enzyme showed peak at 2506 cm⁻¹ which was assigned to the OH stretching of the carboxyl group presented. This peak later appeared after the immobilization of the antibody enzyme on the glutaraldehyde-activated PAN-nfs.

Hydrolyzed PAN-nfs as supports

Zhang et al. [25] performed hydrolysis on PAN-nfs with KOH, NaOH, and LiOH and, subsequently, use them for immobilization of polyethyleneimine (PEI) to form a composite membrane. Bagheri et al. [26] also hydrolyzed PAN-nfs with sodium hydroxide and immobilized thiourea. Jia et al. [27] in their reaction hydrolyzed and chlorinated PAN-nfs before grafting natural polymer on them to improve moisture absorption and water retention properties. Li et al. [28] also synthesized PAN derivative of poly (acrylonitrile–maleic acid) containing reactive carboxyl functionality and fabricated it into fibre and used it to immobilize lipase.

Zhang et al. [29] made use of series of steps to immobilize ligands on PAN nanofibres. The first step involved alkaline hydrolysis with NaOH to generate a surface structure of polyacrylamide and polyacrylic acid. The second step was to further react the same fibre in step one with ethylenediamine (EDA). The carboxylic group of polyacrylic acid was turned into amino end groups. PAN–NaOH ? EDA membrane was further modified with GA and this resulted in aldehyde terminal groups needed for the chemical binding of chitosan (CS) onto the fibre surface. The activated membrane with GA was treated with chitosan (CS) solution. CS was deposited onto the PAN-nfs surface to minimize the fouling concern. Furthermore, CS contains many free amino groups, which could attach dye ligands successfully. For the glucosamine unit in the CS molecule, there is pendant structure due to the reaction of another aldehyde group in the glutaraldehyde molecule with one amino group in the CS molecule and unreacted amino groups in the CS film. The hydroxyl or amino groups of the composite membranes were multiplied after coating CS and can react with the chloride of the triazine ring of the dye Cibacron Blue F3GA (CB) under alkaline conditions, thus giving rise to covalent bonds. The SEM images showed that unmodified PAN-nfs and the PAN-nfs chemically tethered with CS were similar; however, the fibre diameter of the latter increased significantly. The surface of the CB immobilized PAN-nfs became coarser than those of uncoated PAN-nfs.

The FT-IR spectra of dye affinity membranes have some absorption bands different from the pristine PAN-nfs (Fig. 4). The absorption band of the dye affinity membrane at 1230 cm^{-1} corresponds to the stretching vibrations of $-\text{CN}-$ on CB (Fig. 4c), which is also observed in the spectrum of CB (Fig. 4b). The absorption band in the region between 1600 and 1450 cm^{-1} is a characteristic of the benzene ring.

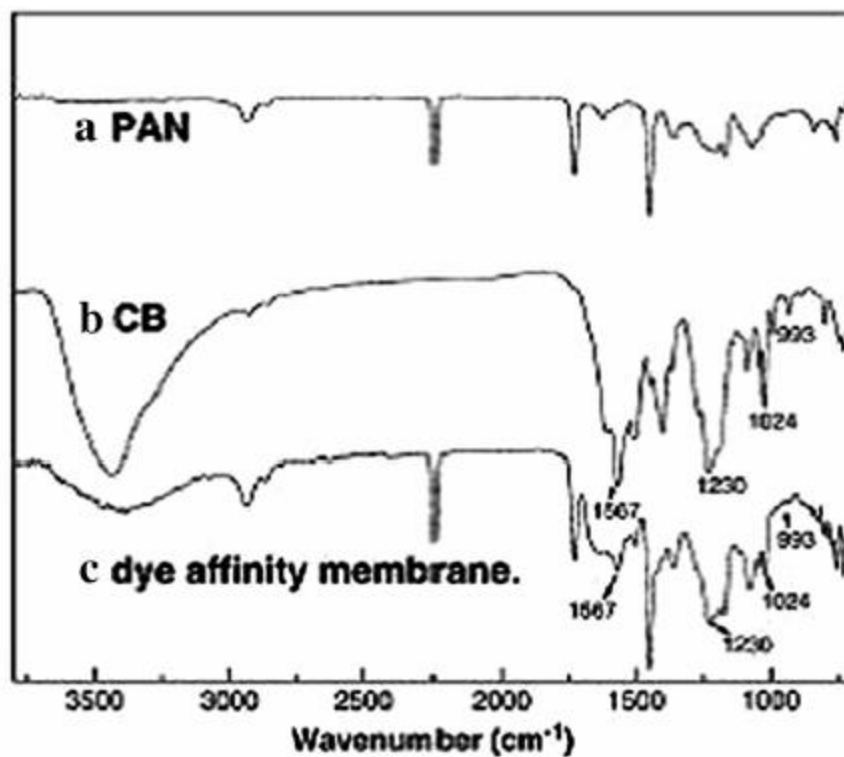


Fig. 4 FT-IR spectra of *a* PAN-nfs, *b* CB, and *c* dye affinity PAN-nfs Zhang et al. [29]

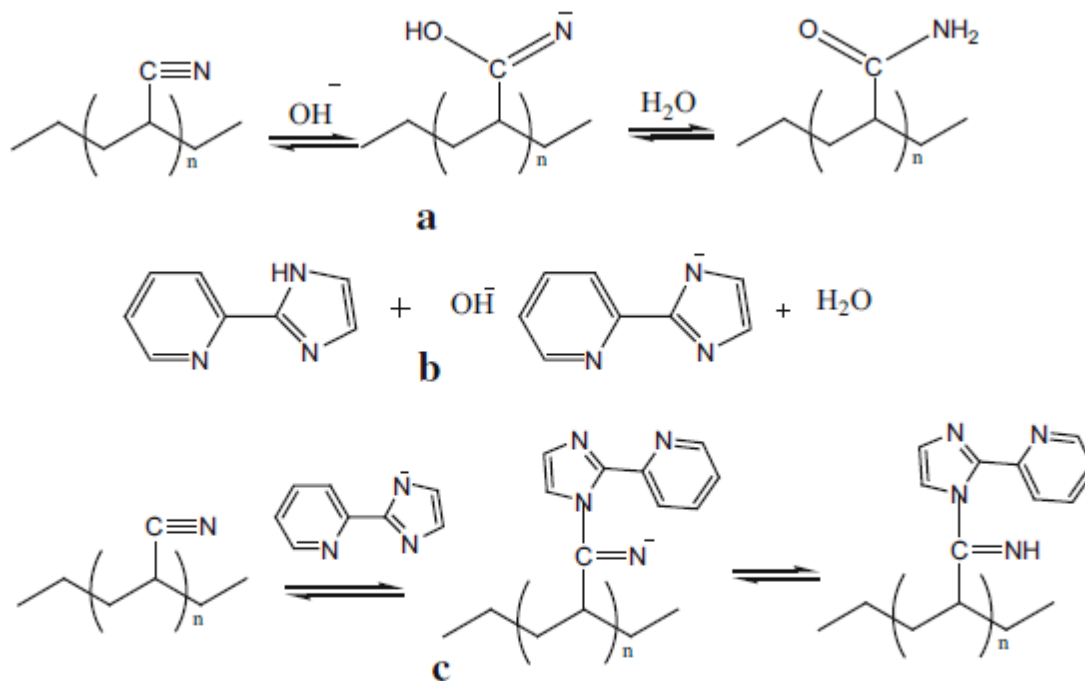


Fig. 5 Surface modification of PAN-nfs using PIM Ndayambaje et al. [32]

On the other hand, the adsorption intensity of dye affinity membrane at 1024 cm^{-1} representing symmetric stretching of S–O and is highly pronounced than that of the pristine PAN-nfs. The data indicated that the coupling of CB is successful [30, 31].

Ndayambaje et al. [32] proposed the reaction for the immobilization of 2-(2¹-pyridyl)imidazole (PIM) on PAN-nfs in the presence of KOH (Fig. 5). The base-catalyzed hydrolysis of the nitrile groups on PAN-nfs to amide occurred (Fig. 5a) alongside the formation of 2-(2¹-pyridyl)imidazolate anions (Fig. 5b). The anions then react with PAN-nfs by nucleophilic attack on the carbon carrying the nitrile group (Fig. 5c) [32].

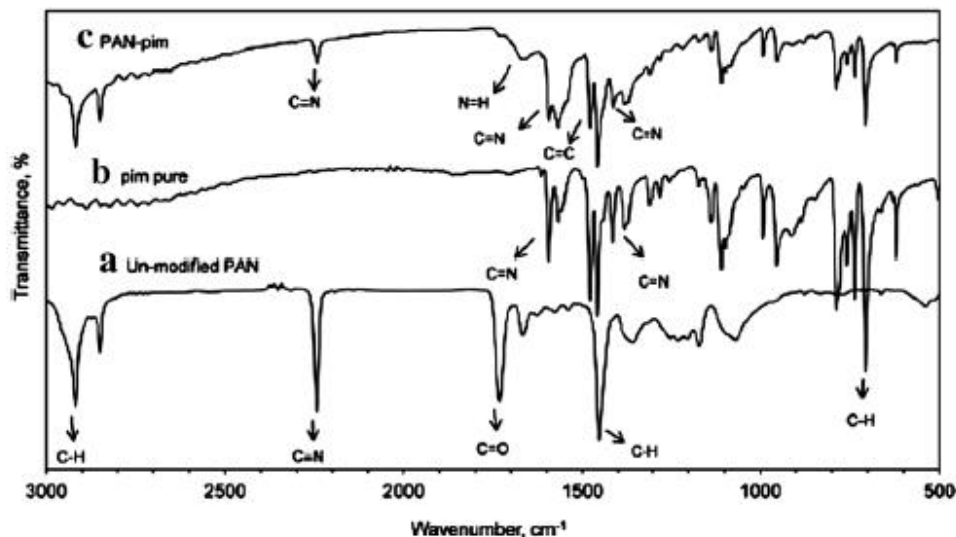


Fig. 6 ATR-FTIR spectra of a Unmodified PAN, b 2-(2¹-pyridyl)imidazole (PIM), and c PAN-PIM Ndayambaje et al. [32]

The ATR-FTIR spectrum (Fig. 6c) showed the decrease in the peak intensity of C:N at 2245 cm^{-1} after immobilization of PIM (Fig. 6b) when compared to pristine the PAN-nfs (Fig. 6a). In addition, the band at 1745 cm^{-1} , which corresponds to C=O, completely disappears after the surface modification reaction of PAN-nfs (Fig. 6c). This was attributed to the hydrolysis of the ester to carboxylate group [33]. The new bands observed at 1675, 1570, and 1395 cm^{-1} (Fig. 6c) are suggesting that both carboxylate and amide groups are formed. Ndayambaje and co-workers [32] suggested that the band at 1675 cm^{-1} can also belong to amidine groups which are known to be the intermediates in base hydrolysis of PAN-nfs [34, 35]. The bands around $1670\text{--}1569\text{ cm}^{-1}$ which were assigned to the C=N and N–H bonds, respectively, in the amidine moiety [11, 32, 36].

Amidoximated PAN-nfs as supports

In advanced oxidation processes with hydrogen peroxide, the use of transition metal cation catalysts is believed to increase the rate of decomposition of hydrogen peroxide to oxidize

pollutants in waste waters. This is based on Fenton's chemistry. The complexes of modified PAN-nfs coordinated with metal ions can, therefore, be used as catalyst. It was reported that the active catalyst sites were formed due to the content of carboxylate ion, amino, imine, and amide groups on the modified PAN fibres, and the metal was primarily distributed on their outer surface [14–16]. Among the surface functionalized PAN-nfs, the fibres containing amidoxime groups have shown a great potential for application due to their high tendency to form strong complexes with a wide range of metal ions as well as their ease of synthesis [14, 37–39].

Ishchenko et al. [15] prepared a heterogeneous Fenton's catalyst with the metal cation fixed to a polyacrylonitrile (PAN) support for decomposition of hydrogen peroxide in aqueous solutions. This catalyst was developed towards the decolourization of dyes in a sample of effluent from the textile industry. The PAN-nfs was functionalized using hydroxylamine and sodium hydroxide as discussed by Ndayambaje et al. [32]. The PAN-nfs were knitted into a mesh before modification to enable easier access of reagents to the fibre surface during modification. The modification parameters were varied so as to optimize the extent to which the metal cation was fixed onto the fibre. The transition metal cations complexes of $\text{Fe}^{3?}$, $\text{Co}^{2?}$, $\text{Cu}^{2?}$, and $\text{Ni}^{2?}$ were produced and were subsequently subjected to treatment with Na_2EDTA solution. The amount of metal remaining on the modified polymer after this treatment was considered to be irreversibly sorbed and firmly fixed on the fibre surfaces.

Amidocimated PAN-nfs (AMPAN-nfs) were also used as a template for the in situ formation of Ag nanoparticles on the specified surface [40]. The AMPAN-nfs produced after 2 h of modification with hydroxylamine was immersed in different concentrations of $\text{Ag}^?$ solution for 24 h. The fibres were washed with distilled water several times to remove the free unchelated $\text{Ag}^?$. The amount of chelated $\text{Ag}^?$ was determined by atomic absorption spectrophotometry. Finally, the fibres were immersed in 7.5 wt% formaldehyde solution to form the AMPAN–Ag nanocomposites. The advantage of this method is that all free Ag ions in solution are removed by washing and the aggregation of the Ag nanoparticles during the reaction is prevented. This approach can be used as template for preparing other metals, metal oxides, metal sulfides, and metal-containing semiconducting materials [40]. The SEM images of AMPAN-nfs and AMPAN-Ag [40] showed a great deposition of $\text{Ag}^?$ on AMPAN-nfs when compared to pristine PAN-nfs. Zhenbang et al. [14] also functionalized PAN-nfs with hydroxylamine and its mixture with hydrazine as discussed earlier and were used for immobilization/complexation of $\text{Fe}^{3?}$. Zhang et al. [41] prepared antibacterial PAN fibres membranes by functionalization of PAN-nfs through amidoximation reaction followed by the coordination of silver ions.

Conclusions

This article has shown that electrospun PAN nanofibres can influence and enhance the behaviour of any material immobilized on them. A proper surface modification pathway must be chosen so as to make a covalent bond between the surface of PAN-nfs and materials

to be immobilized. Moreover, the use of flexible spacers could be an interesting way of making this covalent bond. This is done in most cases when the chemistry between the support and the material could not form a covalent bond or when there is need to extend the arms of the materials on the support. Having said all these, an immobilized material that does not fail leaching test in whatever medium is planned to be used is said to be stable and therefore the synthesis of novel nanomaterial might have been achieved. Meanwhile, many studies lack evidence of regeneration of materials immobilized on PAN-nfs. The various surface-modified methods could be used as supports for biological compounds, organic ligands and transition metal catalysts for various applications. Moreover, immobilization of organic ligands on PAN-nfs through these chemical modifications could be an interesting idea for adsorption of metals from aqueous solutions.

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